The Preparation and Crystal Structure Analysis of Some Halo-Mercury Compounds

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To my friends and family

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Abstract

This thesis mainly deals with the synthesis and X-ray structure analysis of some halo-mercury compounds.

In chapter 1, the published work on the structural chemistry of mercury compounds is described with special reference to the difficulties in determining a van der Waals radius for the metal. The different kinds of Hg···Cl interactions and the upper limit of an effective Hg···Cl interaction are discussed.

In chapter 2, the preparation and structure determination of some compounds containing the anion $Hg_6Cl_{13}^-$ are described. The similarity of this anion to $Hg_5Cl_{11}^-$ and the anionic structure of "$Hg_{5.5}Cl_{13}^{2-}$" is discussed.

Chapter 3 deals with the preparative experimental work of analysing the composition of the double salts of mercuric chloride with ethylenediamine chloride and with cobalt(III) ammonium chloride using the full-range solubility method. The resultant stoichiometries are described and discussed. Using the results obtained from chapter 3, two new ethylenediamine chloro-mercury salts, $[NH_3(CH_2)_2NH_3]_2[HgCl_4][Cl]_2$ and $[NH_3(CH_2)_2NH_3][Hg_2Cl_6]$, were prepared and their X-ray single crystal structures were determined. One contains a $[HgCl_4^{2-}]_n$ chain structure and the second contains $[Hg_2Cl_6^{2-}]$ anions. Their structural characteristics are described and discussed.

Chapter 5 deals with two cobalt(III) chloro-mercury salts of $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$ and *trans*-$[CoCl_2(en)_2]_2[Hg_2Cl_6]$. A new chloro-mercury anionic structure of $[Hg_3Cl_9^{3-}]$ is found in the former and the latter contains the familar $[Hg_2Cl_6^{2-}]$ anion. Their structural characteristics are described and related to the series of anionic structures of $[Hg_3Cl_x^{n-}]$ (X=9, 10, 12).

The cation $[H_4trien]^{4+}$ was investigated in the expectation that a new anion with four negative charges might result. The new compound of

triethylenetetramine chloro-mercury, $[H_4trien][Hg_2Cl_8]$, was prepared and its X-ray single crystal structure is described in chapter 6. It demonstrates the existence of the new anionic structure of $[Hg_2Cl_8^{4-}]$.

In order to assist in a study of the anation kinetics of [*cis*-$PtCl_2(NH_3)_2$] with $HgCl_2$, the X-ray single crystal structure of the adduct of $HgCl_2$ with [*cis*-$PtCl_2(NH_3)_2$] was determined and the correlation between this structure [*cis*-$PtCl_2(NH_3)_2 \cdot (HgCl_2)_3$] and related structures in the literature is illustrated in the chapter 7.

In chapter 8, the major structural results of this project are summarized. The "structure-correlation approach method" is applied to the $HgCl_3^-$ and $Hg_2Cl_6^{2-}$ structural subunits from our work and from the literature in order to determine the upper limit of an effective Hg···Cl interaction. An upper limit of 3.35Å is proposed, based on the analysis of currently available crystallographic data.

Chapter 9 deals with two organomercury(II) complexes: $[(Ph_3P)CHCOPh \cdot HgCl_2] \cdot CH_3OH$ and $[(Ph_3P)CHCOPh \cdot HgI_2]$, and their precursor ligand, $[(Ph_3P)CHCOPh]$. Their X-ray single crystal structures are determined and their structural characteristics are described and discussed. These two organo-mercury compounds are examples in which the Hg atom adopts a distorted tetrahedral coordination geometry. They are also compared with related structures in the literature.

Chapter 1

Review

1.1 Review

The linear structure of mercury chloride $HgCl_2$ was established [1,2] over fifty years ago and since that time there has been considerable interest in the structural chemistry of mercury(II). This is mainly because of the fact that the mercury atom actually does not form regular coordination polyhedra but, on the contrary, polyhedra that are usually irregular in symmetric shape [3]. Also the coordination sphere of mercury(II) usually contains both close and distant bonded atoms [4]. There have been some reviews on the chemistry of mercury(II) compounds published since 1960. Some of the early reviews are still regarded as very important sources in this area.

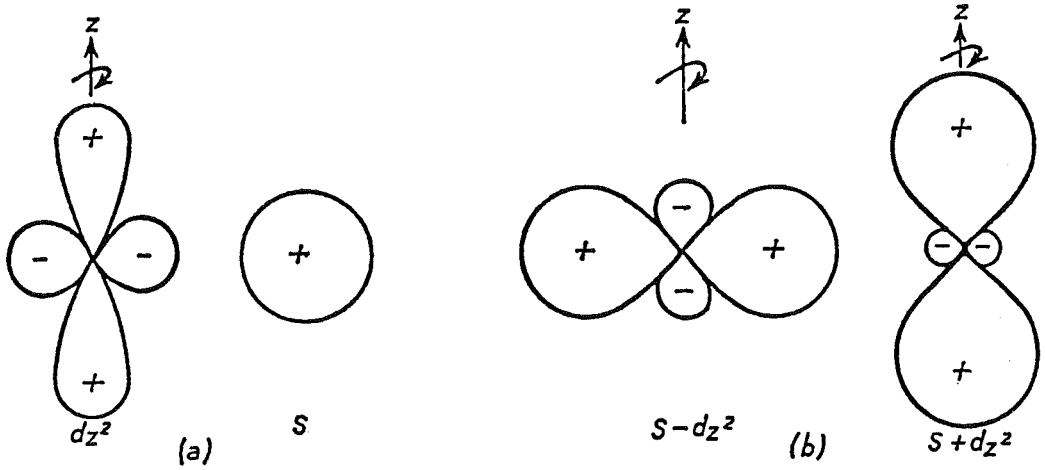
One of the early important reviews by Deacon [5] in 1963 comments on the special properties of mercury with respect to its electron configuration. He stated that mercuric ion has the d^{10} configuration and this spherically symmetrical arrangement is expected to lead to simple stereochemistry. For example, for 2, 3, 4, 5 and 6-fold coordination, the configurations linear, trigonal, tetrahedral, pentagonal-bipyramidal and regular octahedral were expected. He also stated that mercury showed two unusual features. Firstly, two-coordination is more common than for the analogous zinc and cadmium ions and, secondly, there is a tendency for the linear X-Hg-X (X=halogen) arrangement to be retained when further ligands are added. Orgel [6] explained this character of the mercury(II) as follows: (i) Hg(II) often formed sp covalent bonding rather than ionic bonding; (ii) the mechanism of the s-p hybridisation involved d-s mixing. The d-s mixing mechanism, according to Orgel, was perhaps more important for mercury to favour the linear X-Hg-X arrangement. Table 1.1 [6] shows the d-s separation for the common d^{10} ions.

Table 1.1

Energies (e.v.) of lowest d^9s states above the d^{10} ground state

	Cu^+	Zn^{2+}	Ag^+	Cd^{2+}	Au^+	Hg^{2+}	Tl^{3+}
d^9s	2·7	9·7	4·8	10·0	1·9	5·3	9·3

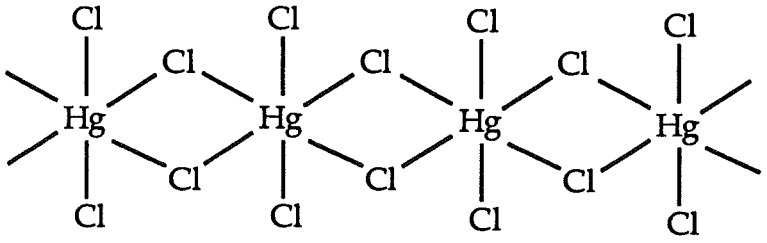
It can be seen that a small d-s separation is always associated with a strong tendency to linear distortion. This is essentially because in order to achieve this d-s mixing, the electrons in the d orbital must be promoted to the next s orbital so that the whole process of promotion and distortion is energetically advantageous only if the d-s separation is sufficiently small. The mixing of d and s orbitals can lead to a charge distribution strongly favouring a linear arrangement by removing charge from the region between the ligands and the metal ion (Scheme 1.1). Scheme 1.1 shows diagrammatically the d and s orbitals and the two d-s hybrids.



Scheme 1.1 (a) the d_{z^2} and s orbitals; (b) the s-d_{z^2} and s+d_{z^2} hybrid orbitals

Hybridisation of the d_{z^2} and s orbitals gives two new orbitals, and mercury can either form two short strong bonds along the z–axis and four weak bonds in the xy–plane, or four strong bonds in the xy–plane and two weak ones along the z–axis, depending on which of the orbitals is filled.

This frequently leads to distorted octahedral stereochemistry for six coordination, and this is borne out by all subseqent work including that reported here. $K_2HgCl_4 \cdot H_2O$ is one of the examples [Scheme 1.2] [7].



Scheme 1.2

$(HgCl_4^{2-})$ in $K_2HgCl_4 \cdot H_2O$

A second important review by Grdenic in 1965 [8] is still regarded as the most cited and authoritative source in this area [3]. In this paper, Grdenic reviewed the structural chemistry of mercury in both molecular and macromolecular compounds. In the first chapter of his review, he suggested that the acceptable radii of mercury, according to currently available X-ray crystal structure data and spectoscopic results [9,10,11], were: metallic radius, 1.50Å≤r(Hg)≤1.73Å; van der Waals radius: r(Hg)=1.50Å; ionic radius: $r(Hg^{2+})$=1.04Å; digonal covalent radius r[Hg(2)]=1.30Å and tetrahedral covalent radius r[Hg(4)]=1.48Å. In addition, he also mentioned that it was difficult to determine the coordination number of mercury in a crystal structure "as for mercury, frequently the distances between the surrounding atoms and mercury do not follow the additivity rule of the atomic radii currently accepted, yet are less than the sum of the van der Waals radii. Even when only atoms of one element surround mercury, markedly different distances may be found." Even over twenty years later, the discussion of what are acceptable radii for mercury is still contentious. In reviewing the coordination chemistry and crystal and molecular structures of mercury compounds he observes that the characteristic

coordination numbers of mercury are 2, 3 and 4 for covalent bonding and 8 for ionic bonding. He stated that one of the main features in the stereochemistry of mercury is a distinctly pronounced tendency of the mercury(II) to form two strong predominantly co-linear bonds. This had been found in most of the mercury(II) compounds by X-ray crystal structure analyses. In the chapter on "Halogenomercurate(II) compounds", he said "The crystal structures of the mercuric halides are an example of a morphotropic transition dependent on the electronegativity of the halogen (4.0, 3.0, 2.8 and 2.5 for F, Cl, Br. and I, respectively)" but "there is one exception to the electronegativity rule conclusion that in chloromercurate the characteristic coordination of mercury should be digonal" and "the configuration of the anion does not follow from the stoichiometry". This last point on chloromercurate has been one of the most interesting areas in our study. In the last chapter of his review, "General Concepts of the Stereochemistry of Mercury", Grdenic stated that "There are two main features in the stereochemistry of mercury which have to be explained: (1) reduction of the characteristic coordination number from six or four (as with zinc and cadmium) to two, and (2) additional ligand approaches leading to distorted effective coordination, generally distorted octahedral." His explaination for both of the phenomena was based on Orgel's [6] d-s mixing theory which we have mentioned before in this chapter. He also pointed out that the arrangement of two short strong bonds in the z–direction and four weak ones in the xy–plane was preferred by mercury.

In 1983, Lyudmila G. Kuzmina and Yury T. Struchkov [3] reviewed "secondary interactions" in their review paper entitled "Structural Chemistry of Organomercury Compounds. Role of Secondary Interaction". In this paper, the structures of the organomercury compounds were reviewed from the point of view of the secondary interactions of mercury atoms with surrounding atoms. These bonds, though variable in length, exhibit a definite influence on the crystal structure which is manifested in

unusual coordination geometries around the mercury atoms. Such interactions are usually refered to as secondary bonds. When taking into account these secondary bonds, the effective coordination of the mercury atom appears to be more complicated. In all cases when a distortion of the characteristic linear coordination of the mercury atom is observed it is considered due to secondary bond formation. From spectroscopic research results and X-ray crystal structure data, the van der Waals radius range for mercury 1.5-2.0Å appears broad. This result is not accidental and implies that representation of the van der Waals surface of the mercury atom by a sphere is very rough. Kuzmina and Struchkov[3] adopted the minimal values 1.5-1.6Å derived for the van der Waals radius of mercury to decide whether a particular distance, mercury to heteroatom, corresponds to a secondary bond. They stated that there is no clear-cut boundary between situations where there is a secondary bond and there is no secondary bond and concluded, in cases of Hg···Cl interactions, the sum of the van der Waals radius of Hg···Cl would lie in the range 3.35-3.45Å.

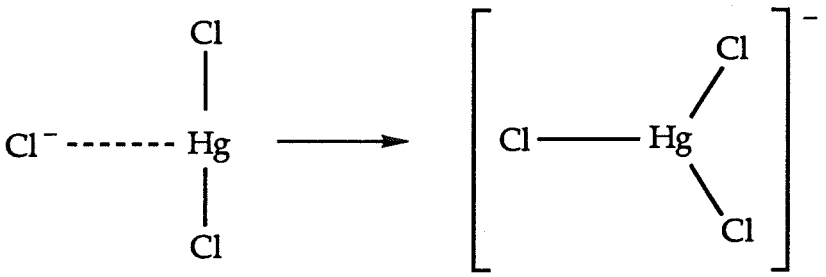
The peculiar feature of chloromercurate in which the configuration of the anions does not follow the empirical stoichiometry has been mentioned in these reviews. It is still a very open topic in structural chemistry of chloromercurate. For example in $K_2HgCl_4 \cdot H_2O$, we can see there are no discrete $HgCl_4^{2-}$ anions but rather columns of distorted $HgCl_6$ octahedra which share two opposite edges, via. bridging Cl atoms [Scheme 1.2]. Now there are over 15 examples of $HgCl_4^{2-}$ anions for which a variety of structures have been established.

As we have mentioned before, an acceptable van der Waals radius for mercury is elusive but lies in the range 1.5-2.0Å. Thus in view of the structural diversity exhibited by chloromercury(II) systems, a distinction between bonded and non-bonded atoms surrounding Hg(II) is not always clear [12]. This is because the sum of the covalent radii is also not well defined[13] with estimates varying from 3.17 to 3.53Å [14] and the effective

covalent radius of Hg(II) may well depend on the stereochemistry adopted [8]. Grdenic proposed to use the value of 1.73Å, ie, a half of the next short interatomic distance in the metal mercury crystal for estimation of the specific interactions in his review even though he suggested that the van der Waals radius of mercury was 1.5Å which is equal the metal radius of the mercury atom. He also suggested that we should consider the distances between1.50Å and 1.73Å plus the van der Waals radius of the adjacent donor atom as non-bonding interaction. Canty and Deacon [15] suggested that the van der Waals radius of mercury was in the range of 1.7-2.0Å on the basis of analysis of the inter- and intra- molecular distances Hg···Hg, Hg···N, Hg···Cl, Hg···O [16,17,18,19] in many crystal structures. Thus the van der Waals radius range for mercury is very wide, from 1.5-2.0Å. Kuzmina and Struchkov [3] suggested in their review that the van der Waals radius of mercury was 1.5-1.6Å and this was also used to decide whether a particular distance on mercury-heteroatom interaction corresponded to a secondary bond. For the chlorine atom, it seems that the van der Waals radius is not as complicated as for mercury. The distance of 3.6Å was usually considered to be the upper limit of equilibrium van der Waals interactions between two chlorine atoms [120]. Desiraju [20] stated that there has been much discussion on the existence and nature of short (3.2-3.6Å) Cl···Cl non-bonded contacts in molecular crystals. He discussed a few different types of Cl···Cl interactions in his paper, in particular the "Attractive nature of Cl···Cl contacts". He concluded, from some experimental results, that Cl···Cl contacts must be attractive. Desiraju has also discussed the packing motifs of some chloro compounds in crystal structures. The range of values for the shortest Cl···Cl contacts in crystal structures depend on the type of the crystal structures, according to him. For example, in the group of β-structures, the range of the values for the shortest Cl···Cl contacts is from 3.27-4.10Å [20]. Kuzmina and Struchkov [3] suggested, on the basis of the radii of mercury and chlorine, that the sum of the van der Waals radii for Hg···Cl was 3.35-

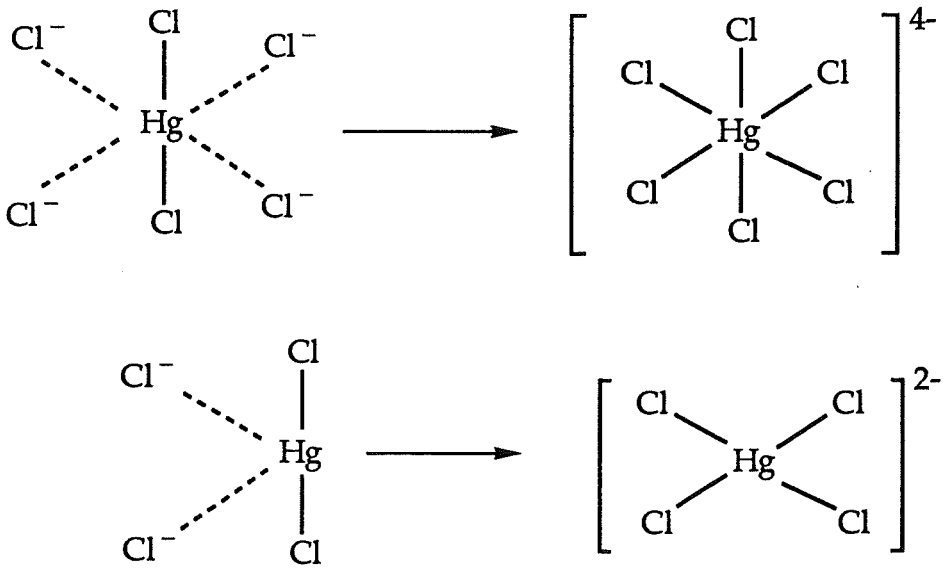
3.45Å, and these were considered to be Hg···Cl secondary bonding interaction distances.

In view of these uncertainties, the structure-correlation approach of Burgi and Dunitz [21, 22] has been introduced to the Cl-Hg-Cl+Cl⁻ interaction system. In this approach, the observed Cl-Hg-Cl angle is plotted against the approaching Hg-Cl distance for structural fragments containing one distorting chloro ligand [Scheme 1.3].



Scheme 1.3

Extrapolation of this correlation to 180° for the Cl-Hg-Cl angle shows that a distance greater than 3.0Å for the third chloro ligand will be effectvely non-bonding.



Scheme 1.4

Ben Salah, et al [23], have also tried similar plots using $HgCl_2 + 2Cl^- \rightarrow HgCl_4^{2-}$ and $HgCl_2 + 4Cl^- \rightarrow HgCl_6^{4-}$ data where the average of the two longer Hg-Cl bonds is plotted against the average of the two shorter Hg-Cl bond [Scheme 1.4].

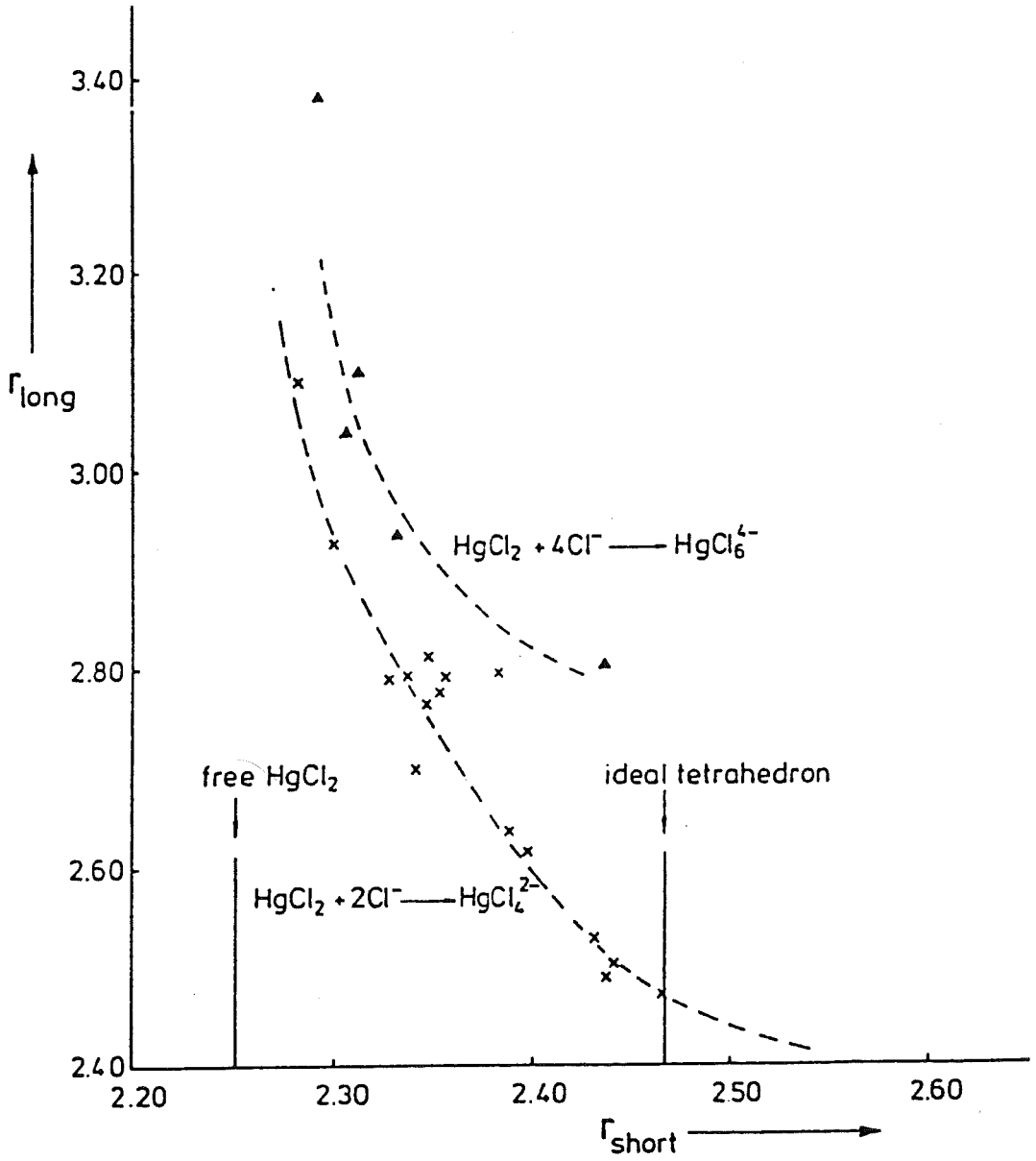
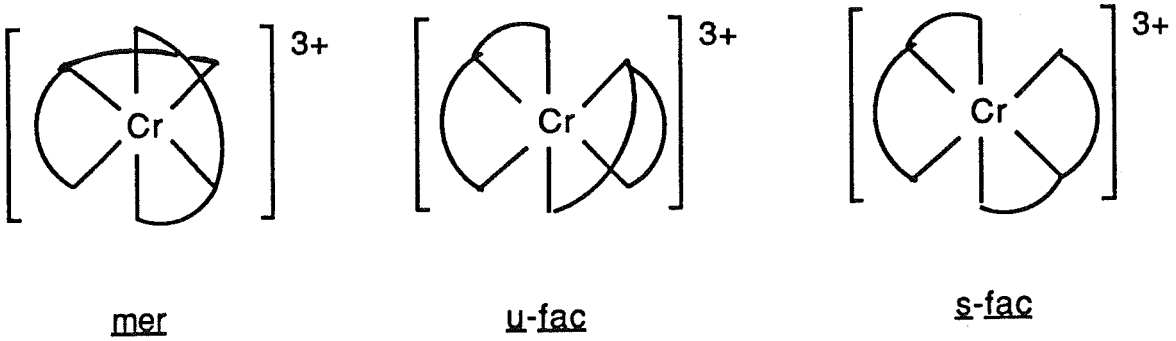


Figure 1.1 Correlation diagram showing the average value of the longer Hg-Cl bonds as a function of the average value of the shorter Hg-Cl bonds for the fourfold coordinated (x) and the sixfold coordinated (▲) Hg(II) complexes

Although their plots were scattered and curved, with individual points showing considerable scattering, two reaction pathways were clearly visible (Figure 1.1). The curve describing $HgCl_2+2Cl^-\rightarrow HgCl_4^{2-}$ shows intermediate complexes all the way from an isolated $HgCl_2$ group to an ideal tetrahedron. The second one only describes limited range for the reaction $HgCl_2+4Cl^-\rightarrow HgCl_6^{4-}$ and did not approach an idealized octahedron. Thus they concluded that "Hg-Cl bond lengths of the order of 3.0-3.2Å appear to give non-negligible contribution to the bonding in these complexes" but they did not give the upper limit.

The angle deformation method has been considered as one of the most sensitive indications for Hg-Cl interactions. In our work we will consider interaction distances of Hg-Cl up to 3.35Å, which is a value close to the estimated the sum of the van der Waals radii of Hg···Cl.

The interest in this area in this laboratory arose from a study of the $Cr(dien)_2^{3+}$ system [24], where 3 topological isomers are possible [Scheme1.5]. The normal synthetic route could lead to a mixture of the three topological $[Cr(dien)_2]Cl_3$ isomers and preliminary chromatographic investigations [25, 26] showed that at least one of them was quickly hydrolysed[27] in aqueous solution.



mer u-fac s-fac

Scheme 1.5

Several anions were investigated in an attempt to produce salts suitable for single crystal structural analysis. It was not until the possiblity of an $HgCl_5^{3-}$ [28, 29] was explored by crystallisation of the trivalent cation mixture from 3M HCl with $HgCl_2$ solution that any progress was achieved. This provided the required breakthough and crystals suitable for preliminary X-ray study were obtained. Actually all three isomeric cations contained $Hg_2Cl_7^{3-}$ salts rather than the expected $HgCl_5^{3-}$ salts. Consequently, X-ray structural data were of interest, not only to characterise the polyamine topology in the cation but also to establish the nature of the unusual $Hg_2Cl_7^{3-}$ anion.

During the course of coping with the difficulties of the $[Cr(dien)_2]Hg_2Cl_7$ system, the work on the investigation of the $Hg_xCl_y^{n-}$ anion system was established and it has been proved that it is worthwhile.

This thesis describes our attempts to identify and prepare crystals of a wide range of stoichiometries containing chloromercury(II) anions of diverse stereochemistry. Where possible structures have been established using X-ray single crystal structure determinations. Because the same laboratory equipment and computers were used for all these studies we are describing all the procedures common to these analyses in the next section. The atomic coordinates and thermal parameters for each structure are collected together with their numbering schemes in appendix A. Tables of interatomic distances and bond angles are given in each individual chapter. Thus the sections dealing with each structure separately concentrate on factors peculiar to each analysis and discussion of the revealed stereochemistry.

1.2 General Crystallography

Crystals suitable for X-ray single crystal structure analysis were obtained as described in the Experimental Section of each chapter. X-ray crystallographic data were collected on a Nicolet R3m four-circle

diffractometer using graphite-monochromated MoKα radiation (λ=0.71069Å). The cell parameters were determined by least squares refinement of 20 to 24 accurately centered reflections in the range $5°<2\theta<36°$. During the data collection the crystal stability was monitored by recording three standard reflections every 97 reflections and no significant variations were observed for any data sets. The collected intensities were corrected for Lorentz and polarisation effects and the absorption correction was applied based on Ψ-scan data. Reflections stronger than $3\sigma(I)$ are used in the structure analysis. Hydrogen atoms were inserted at calculated positions using a riding model with fixed thermal parameters. The function minimised in the refinement was $\Sigma(w\,|F_o|-|F_c|)^2$ where $w=[\sigma^2(F_o)+gF_o^2]^{-1}$. All programs used in data reduction and final refinement were contained in the SHELXTL (version 4.0) package [30]. SHELXTL or SHELXS [31] programs were employed to solve the structures, and in some cases the intermediate refinement was performed using SHELX76 [32].

Chapter 2

Preparation and Crystal Structure Determination of Compounds Containing $Hg_6Cl_{13}^-$ Anion

2.1 Introduction

In this laboratory, at least 20 complex anions containing mercury and chlorine atoms have been distinguished in as many separate crystal structure analyses. Empirical stoichiometries may disguise widely differing structural arrangements, for example in $[(HgCl_2)_nCl^-]$ and $[(HgCl_4^{2-})_n]$. Neutral $HgCl_2$ entities forming linked clusters around single Cl^- anions with unusual stoichiometries $[(HgCl_2)_nCl^-]$, have been found for $[Hg_2Cl_5^-]$, $[Hg_3Cl_7^-]$, $[Hg_5Cl_{11}^-]$ and $[Hg_6Cl_{13}^-]$.

$[Et_4N][Hg_nCl_{2n+1}]$ salts were prepared by Reedjik[33] by crystallisation of the appropriate stoichiometric mole ratio of Et_4NCl and $HgCl_2$ from hot acetonitrile. In this laboratory some single crystals of this series suitable for X-ray structure determination were obtained by evaporation of acetonitrile solution containing the stoichiometric amounts of Et_4NCl and $HgCl_2$ at room temperature.

Crystals of $[M^+][Hg_5Cl_{11}^-]$ ($M=NH_4$, Cs, Rb) suitable for X-ray structure analysis were obtained by evaporation of aqueous solution of $MCl:HgCl_2$ in a 1:5 mole ratio at room temperature. The anion $Hg_5Cl_{11}^-$ has been reported and described[34] in the structure of $TlHg_5Cl_{11}$ previously. It is monoclinic and isomorphous with the $[NH_4^+]$, $[Rb^+]$ and $[Cs^+][Hg_5Cl_{11}^-]$ studied here. The similarity of the cell dimensions of all these compounds is apparent in Table 2.1.

Table 2.1 Unit Cell Dimensions for MHg_5Cl_{11} Salts (monoclinic, C2/m)

M^+	a(Å)	b(Å)	c(Å)	β(°)	V(Å^3)	Ionic Radius[121]
NH_4	11.791(1)	14.197(1)	6.505(1)	118.74(6)	954.8(5)*	1.48
	11.685(5)	14.076(5)	6.457(2)	118.59(3)	932.5(5)#	1.48
Cs	11.889(1)	14.268(1)	6.676(1)	119.93(5)	981.4(3)*	1.69
	11.875(4)	14.264(3)	6.667(2)	119.91(2)	978.9(5)#	1.69
Rb	11.782(1)	14.187(1)	6.523(1)	118.94(5)	954.2(4)*	1.48
	11.665(3)	14.040(3)	6.493(3)	118.76(2)	932.1(4)#	1.48
Tl	11.716(1)	14.150(1)	6.460(1)	118.55(5)	940.7(6)*	1.40
K	11.718(2)	14.115(3)	6.442(1)	118.48(20)	936.6(20)*	1.33

*: Reference [34]. Data were collected at room temperature.

#: This work. Data were collected at 193K.

Structurally the $Hg_5Cl_{11}^-$ anion can be regarded as $Cl^-[HgCl_2]_4[HgCl_2]$ or $[Hg_4Cl_9^-][HgCl_2]$. Figures 2.1**a** and 2.1**b** show the common structure of these anions and their packing in the crystal structures.

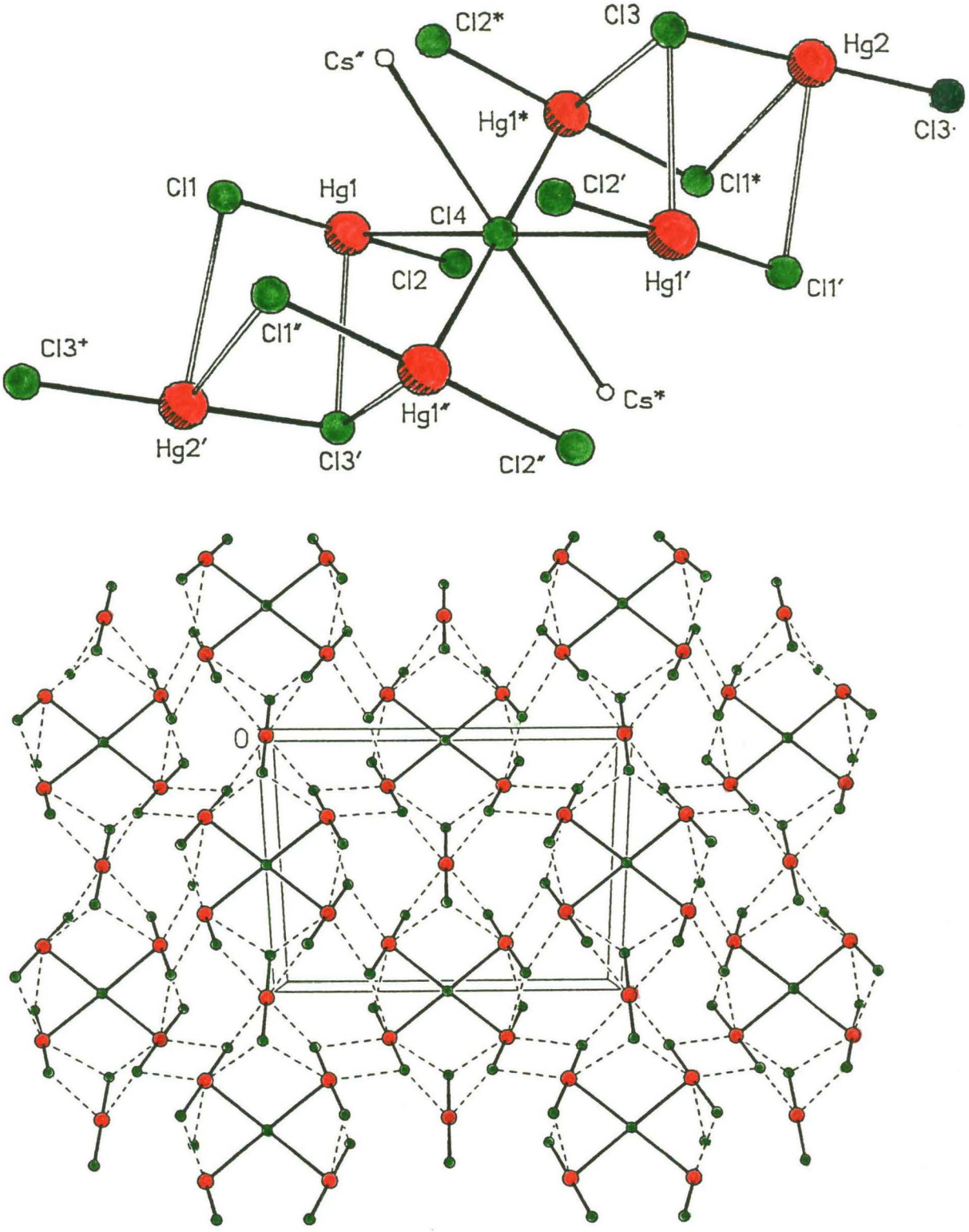


Figure 2.1 The labelling scheme (**a**) and the packing diagram (**b**) for $CsHg_5Cl_{11}$

Table 2.2 Crystal data for the three compounds containing $Hg_5Cl_{11}^-$ anion

Complex	$CsHg_5Cl_{11}$	$RbHg_5Cl_{11}$	$(NH_4)Hg_5Cl_{11}$
Formula weight	1528.5	1481	1413.5
Space group	monoclinic, C2/m	monoclinic, C2/m	monoclinic, C2/m
a(Å)	11.875(4)	11.665(3)	11.685(5)
b(Å)	14.264(3)	14.040(3)	14.076(5)
c(Å)	6.667(2)	6.493(1)	6.457(2)
β(°)	119.91(2)	118.76(2)	118.59(3)
V(Å^3)	978.9(5)	932.1(4)	932.5(5)
Z	2	2	2
$D_{calc(g/cc)}$	2.59	2.64	2.52
Temperature (K)	193	193	193
F(000)	1284	1248	1196
Linear absorption coefficient (cm^{-1})	54.3	57.2	57.0
Transmission factors	0.148, 0.963	0.176, 0.921	0.156, 0.429
Merge	0.121	0.149	0.117
Scan mode	ω	ω	ω
Data collected	±h, k, l	h, k, ±l	h, k, ±l
$2\theta_{max}$(°)	50	55	52
Reflections measured	1977	1217	965
Reflections with I≥3(σ)	637	841	811
Parameters refined	19	19	38
Weighting (gx10^3)	6	6	6
GOOF	4.69	5.19	4.20
R	17.7	14.5	12.1
Rw	16.7	14.1	11.9

Crystal data for the three compounds containing $Hg_5Cl_{11}^-$ in our study are listed in Table 2.2.

If attention is focussed on the chlorine atom at the origin of the projection (Figure 2.1**b**) it can be seen to be surrounded by four $HgCl_2$ molecules with the Hg-Cl distances Hg1-Cl1 2.296(6)Å and Hg1-Cl2 2.288(6)Å, respectively. The distance from this central chlorine atom to each Hg atom is 3.054Å and these $HgCl_2$ molecules are not strictly linear (Cl-Hg-Cl 178.4(4)°). There are longer Hg···Cl interactions with similar neighbouring $[Hg_4Cl_9^-]$ anionic units and with another neutral $HgCl_2$ molecule. In figure 2.1**a** a fragment of this structure is selected to show the location of the counter cations with respect to the central chlorine atoms of the $[Hg_5Cl_{11}^-]$ groups.

As part of our continuing investigation of chloro-mercury(II) anions which have the empirical stoichiometry $[Hg_nCl_{2n+1}^-]$, we prepared and studied the compounds of $[Et_4N][Hg_6Cl_{13}]$ and $[Me_4N][Hg_6Cl_{13}]$.

2.2 Experimental

2.2.1 Preparation of Crystals Containing the $Hg_6Cl_{13}^-$ Anion

Single crystals of $(Et_4N)Hg_6Cl_{13}$ and $(Me_4N)Hg_6Cl_{13}$ were obtained by evaporation a solution containing a 1:6 mole ratio of Et_4NCl(Me_4NCl) and $HgCl_2$ in acetonitrile. One of the corresponding bromides, $[Et_4N][Hg_6Cl_{12}Br]$ was similarly prepared. Its structure proved isomorphous with the chloride and was not pursued.

2.2.2 X-ray Crystal Determination

Crystal data for the two chlorides are listed in Table 2.3. Intensity data for $(Et_4N)Hg_6Cl_{13}$ and $(Me_4N)Hg_6Cl_{13}$ were collected at -120°C using a Nicolet R3m four-circle diffractometer. Graphite monochromated MoKα radiation (λ=0.71069Å) was used with fixed speed omega scans.

Table 2.3 Crystal data

Complex	$(Me_4N)Hg_6Cl_{13}$ (1)	$(Et_4N)Hg_6Cl_{13}$ (2)
Molecular formula	$C_4H_{12}NHg_6Cl_{13}$	$C_8H_{20}NHg_6Cl_{13}$
Formula weight	1738.4	1794.4
Crystal size (mm)	0.28x0.24x0.58	0.34x0.36x0.40
Space group	Hexagonal $R\bar{3}$	Hexagonal $R\bar{3}$
a(Å)	12.911(3)	13.589(4)
b(Å)	12.911(3)	13.589(4)
c(Å)	28.348(7)	28.496(4)
V(Å^3)	4100(2)	4556(3)
Z	6	6
$D_{calc(g/cc)}$	4.23	3.92
Temperature(K)	153	153
F(000)	4944	5088
Linear absorption coefficient (cm^{-1})	350.54	313.98
Transmission factors	0.549	0.628
	0.958	0.780
Merge	0.054	0.053
Scan mode	ω	ω
Data collected	h, k, ±l	h, k, ±l
$2\theta_{max}(°)$	52	52
Reflections measured	2044	2996
Reflections used	1217	1107
Paremeters refined	29	52
Weighting (gx10^3)	6	6
GOOF	2.35	2.42
R	7.92	8.28
R_w	7.90	8.61

The structures were solved using the conventional Patterson and Fourier method and refined by blocked-cascade least-squares procedures. The mercury and chlorine atoms were refined with anisotropic thermal parameters. The cations of both structures were disordered so that the $(Et_4N)^+$ and $(Me_4N)^+$ moeties could not be defined properly. Figure 2.2 is a

perspective diagram of the $Hg_6Cl_{13}^-$ anion. It defines the atom labelling scheme used for each of the two, crystallographically independent, anions in the structure. Table 2.4 lists the coordinates of all the independent non-hydrogen atoms for $(Et_4N)Hg_6Cl_{13}$ and the derived interatomic distances and bond angles also for $(Et_4N)Hg_6Cl_{13}$ are contained in Tables 2.5 and 2.6.

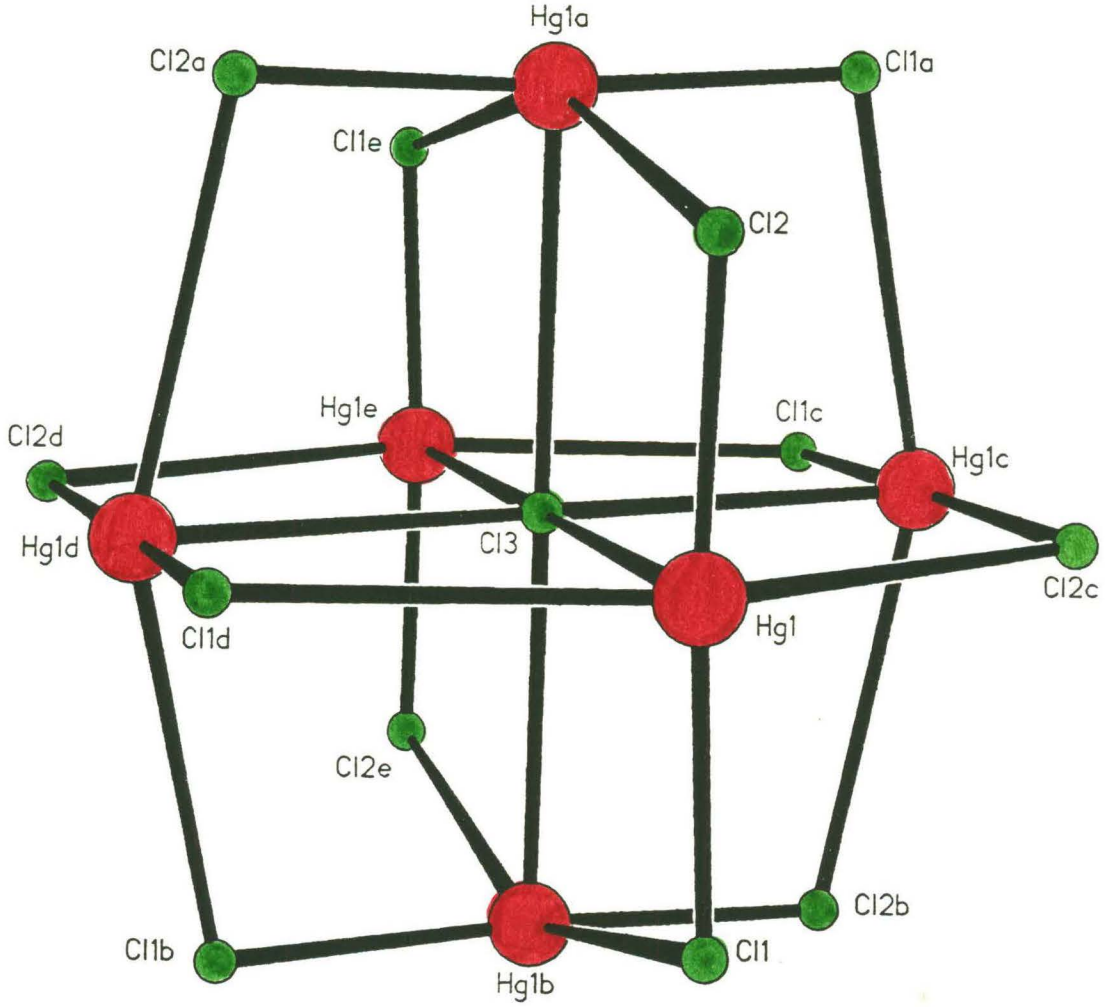


Figure 2.2 The perspective diagram of the $Hg_6Cl_{13}^-$ anion

for $[Et_4N][Hg_6Cl_{13}]$

Table 2.4 Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2 x10^3$)

	x	y	z	U(eq)
Hg(1)	1692(1)	4790(1)	2285(1)	13(444)
Cl(3)	3333	6667	1667	0(4)
Cl(1)	3120(8)	4870(8)	2758(3)	16(2)
Cl(2)	167(9)	4519(9)	1831(4)	29(2)
Hg(2)	1142(2)	9064(1)	615(1)	22(1)
Cl(6)	0	0	0	9(6)
Cl(4)	1898(14)	10659(11)	1071(4)	57(8)
Cl(5)	545(8)	7432(8)	193(3)	18(4)
N	6667	3333	383(45)	802(326)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 2.5 Bond lengths (Å)

Hg(1)-Cl(3)	2.982 (2)	Hg(1)-Cl(1)	2.320 (11)
Hg(1)-Cl(2)	2.312 (12)	Cl(3)-Hg(1A)	2.983 (2)
Cl(3)-Hg(1B)	2.983 (2)	Cl(3)-Hg(1C)	2.983 (2)
Cl(3)-Hg(1D)	2.982 (1)	Cl(3)-Hg(1E)	2.984 (1)
Hg(2)-Cl(4)	2.284 (13)	Hg(2)-Cl(5)	2.286 (10)
Hg(2)-Cl(6A)	3.012 (2)	Cl(6)-Hg(2A)	3.012 (2)
Cl(6)-Hg(2B)	3.012 (2)	Cl(6)-Hg(2C)	3.012 (2)
Cl(6)-Hg(2D)	3.012 (2)	Cl(6)-Hg(2E)	3.012 (2)
Cl(6)-Hg(2F)	3.012 (2)		

Table 2.6 Bond angles (°)

Cl(3)-Hg(1)-Cl(1)	93.1(2)	Cl(3)-Hg(1)-Cl(2)	91.9(2)
Cl(1)-Hg(1)-Cl(2)	174.3(4)	Hg(1)-Cl(3)-Hg(1A)	180.0(1)
Hg(1)-Cl(3)-Hg(1B)	88.6(1)	Hg(1A)-Cl(3)-Hg(1B)	91.4(1)
Hg(1)-Cl(3)-Hg(1C)	91.4(1)	Hg(1A)-Cl(3)-Hg(1C)	88.6(1)
Hg(1B)-Cl(3)-Hg(1C)	180.0(1)	Hg(1)-Cl(3)-Hg(1D)	88.6(1)
Hg(1A)-Cl(3)-Hg(1D)	91.4(1)	Hg(1B)-Cl(3)-Hg(1D)	88.6(1)
Hg(1C)-Cl(3)-Hg(1D)	91.4(1)	Hg(1)-Cl(3)-Hg(1E)	91.4(1)
Hg(1A)-Cl(3)-Hg(1E)	88.6(1)	Hg(1B)-Cl(3)-Hg(1E)	91.4(1)
Hg(1C)-Cl(3)-Hg(1E)	88.6(1)	Hg(1D)-Cl(3)-Hg(1E)	180.0(1)
Cl(4)-Hg(2)-Cl(5)	173.4(6)	Cl(4)-Hg(2)-Cl(6A)	90.7(5)
Cl(5)-Hg(2)-Cl(6A)	95.5(3)	Hg(2A)-Cl(6)-Hg(2B)	180.0(1)
Hg(2A)-Cl(6)-Hg(2C)	89.5(1)	Hg(2B)-Cl(6)-Hg(2C)	90.5(1)
Hg(2A)-Cl(6)-Hg(2D)	90.5(1)	Hg(2B)-Cl(6)-Hg(2D)	89.5(1)
Hg(2C)-Cl(6)-Hg(2D)	180.0(1)	Hg(2A)-Cl(6)-Hg(2E)	89.5(1)
Hg(2B)-Cl(6)-Hg(2E)	90.5(1)	Hg(2C)-Cl(6)-Hg(2E)	89.5(1)
Hg(2D)-Cl(6)-Hg(2E)	90.5(1)	Hg(2A)-Cl(6)-Hg(2F)	90.5(1)
Hg(2B)-Cl(6)-Hg(2F)	89.5(1)	Hg(2C)-Cl(6)-Hg(2F)	90.5(1)
Hg(2D)-Cl(6)-Hg(2F)	89.5(1)	Hg(2E)-Cl(6)-Hg(2F)	180.0(1)

2.3 Results and Structure Description

2.3.1 $(Et_4N)^+$ and $(Me_4N)^+$ cations

From Table 2.2, we can see that the cell dimensions for $(Me_4N)Hg_6Cl_{13}$ are slightly smaller than those for $(Et_4N)Hg_6Cl_{13}$ as would be expected because the methyl group is smaller that ethyl group. However there is an uncharacterised cation disorder problem in both of the structures which has lead to somewhat higher estimated standard deviations than would normal in analyses of this kind.

2.3.2 $Hg_6Cl_{13}^-$ Anions

Crystal structure analyses show that there are two topologically identical, crystallographically independent, anions in this structure (Figure 2.3).

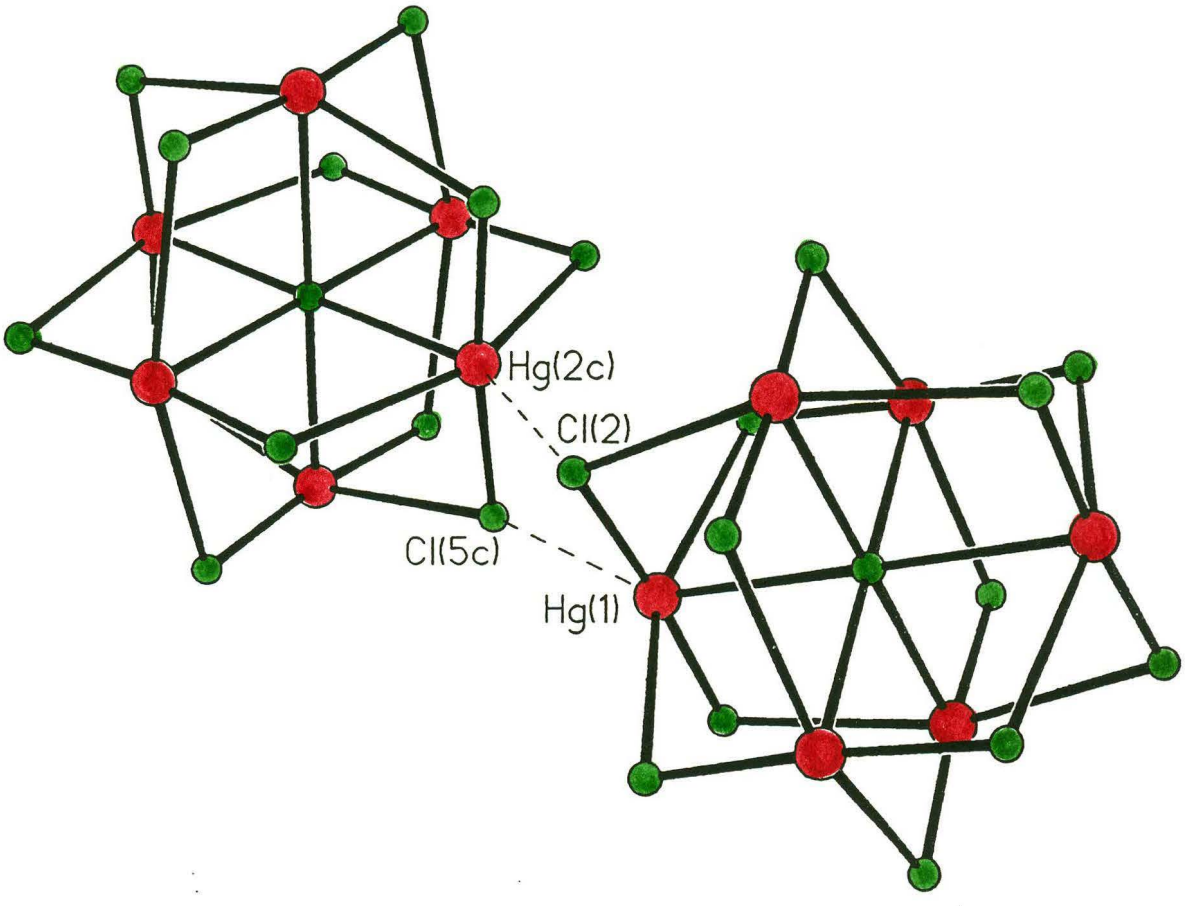


Figure 2.3 The two topologically identical, crystallographically independent, $Hg_6Cl_{13}^-$ anions in this structure

It is shown in Figure 2.2 that the $Hg_6Cl_{13}^-$ can be described as a central chloride ion [Cl(3) or Cl(6)] with six fold symmetry related, coordinated $HgCl_2$ units. In the two $Hg_6Cl_{13}^-$ anions (Figure 2.3), the two short Hg-Cl bond distances within these $HgCl_2$ units are Hg(1)-Cl(1) 2.312(13)Å, Hg(1)-Cl(2) 2.322(11)Å, and Hg(2)-Cl(4) 2.286(13)Å, Hg(2)-Cl(5) 2.286(10)Å with the bond angles Cl(1)-Hg(1)-Cl(2) 174.2(4)° and Cl(4)-Hg(2)-Cl(5) 173.2(6)°, respectively. The distances of mercury atoms to central chlorine atoms are Hg(1)-Cl(3) 2.982(2)Å and Hg(2)-Cl(6) 3.012(2)Å, respectively. Though much longer than 2.30Å, they are shorter than the sum of van der Waals radii for Hg and Cl atoms (3.3-3.4Å), and must be considered to represent bonding interactions, albeit weak. There are also some other weak links between Hg and Cl atoms. The intraanionic Hg-Cl interactions, at 3.18 and 3.34Å for anions (1) and (2) respectively, closely match the interanionic Hg-Cl distances involving the same Cl atoms at 3.17 and 3.32Å. Thus it appears that these Cl atoms prefer to be equidistant from a mercury atom of their own anion and the neighbouring anions. These interanionic links are 0.17 to 0.34Å longer than the link between the central chloride ion and its octahedral Hg neighbours (3.0Å), thus we feel justified in describing the structure as an infinite three dimensional network of weakly connected $Hg_6Cl_{13}^-$ anionic polyhedra with counter cations in the cavities between them (Figure 2.4). In both structures these cavities seem sufficiently large to permit considerable disorder in the counter cations which it was not possible to characterize accurately. As can be shown from the packing diagram, the central aggregate of anionic units is linked through these secondary interactions to form polymeric structures. These secondary inter- and intra- anionic interactions are shown clearly as broken lines in the packing diagram (Figure 2.4). It is also shown that every eight of the $Hg_6Cl_{13}^-$ anions form a big cage and $[Et_4N^+]$ or $[Me_4N^+]$ cations exist inside of these cavities. In order to make the packing diagram show this clearly,

we omit the $Hg_6Cl_{13}^-$ anion on the top of the cage which would overlap the bottom one.

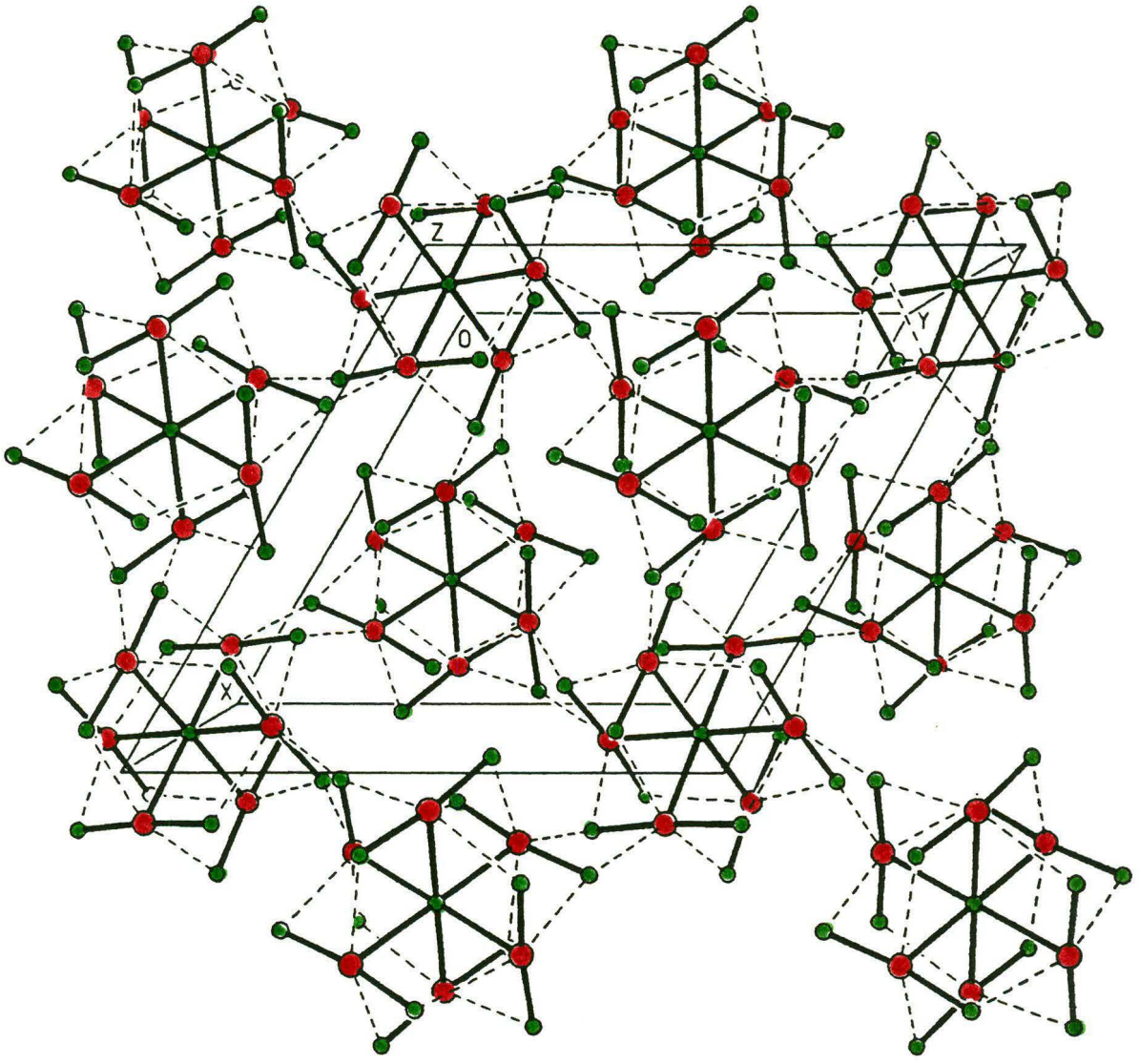
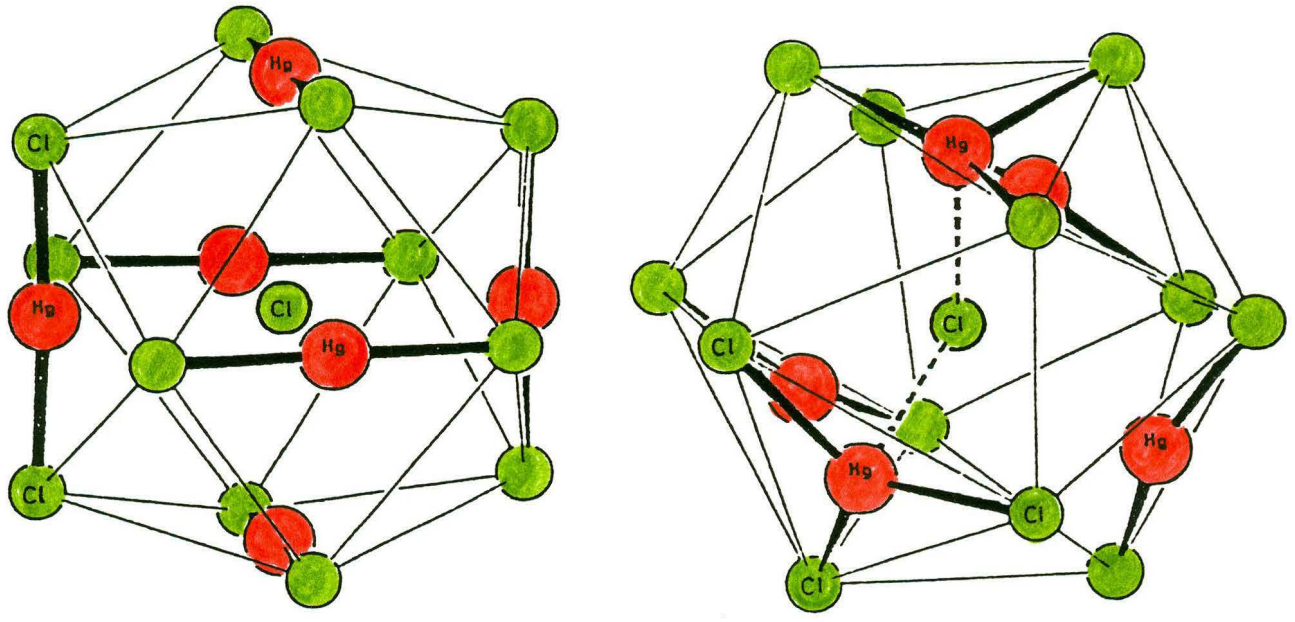


Figure 2.4 The packing diagram of $Hg_6Cl_{13}^-$ anions in this structure

The structure of the $Hg_6Cl_{13}^-$ anion can be related to that of the $Hg_4Cl_9^-$ anion with trans $HgCl_2$ unit added (Figure 2.1). Both consist of a central chloride ion with six and four coordinated $HgCl_2$ units, respectively. In the $Hg_5Cl_{11}^-$ anion, the central chlorine atom has two cations Cs^+ (Rb^+ or NH_4^+) as near neighbours which neutralize the total local anionic charge. For the $Hg_6Cl_{13}^-$ anion, however, the central chlorine atoms do not have any Et_4N^+ (Me_4N^+) cations as neighbours. These cations lie between the complete $Hg_6Cl_{13}^-$ anionic cages as shown (Figure 2.4).

The $Hg_6Cl_{13}^-$ anion also occurs in an interesting complicated structure reported by Thiele and Putzas[35]. They mixed $CaCl_2 \cdot nH_2O$ with $HgCl_2$ in the mole ratio of 1:5.5 in water and obtained the crystals of $CaHg_{5.5}Cl_{13} \cdot 8H_2O$. The anions of $CaHg_{5.5}Cl_{13} \cdot 8H_2O$ consist of a mixture of $Hg_6Cl_{13}^-$ and $Hg_5Cl_{13}^{3-}$ (Figure 2.5).



$Hg_6Cl_{13}^-$ anion $\qquad$ $Hg_5Cl_{13}^-$ anion

Figure 2.5 The structures of $Hg_6Cl_{13}^-$ and $Hg_5Cl_{13}^{3-}$ anions

The $Hg_6Cl_{13}^-$ anion in this crystal structure is very similar to that we have found on its own in $(Et_4N)Hg_6Cl_{13}$ and $(Me_4N)Hg_6Cl_{13}$. Their peculiar stoichiometry appears essential to achieve electrical neutrality using the simple Ca^{2+} cation. They also report analogous bromide and iodide compounds which are not isomorphous with the chloride one. We limit our comparison to the chloride compound $CaHg_{5.5}Cl_{13}\cdot 8H_2O$ only here. In Thiele, et al's report on $Hg_6Cl_{13}^-$ anion, the mercury atoms lie in the two fold-axis for $HgCl_2$ and the two chlorine atoms are related to each other by the symmetry operation. The Hg-Cl distance is 2.284(5)Å with the bond angle Cl-Hg-Cl 176.7(3)° within these $HgCl_2$ units and the distance of mercury atoms to the central chlorine atom is 3.074(4)Å. However in our case the two chlorine atoms within the $HgCl_2$ units are not related to each other but rather exist independently. The Hg-Cl distances within $HgCl_2$ units range 2.286-2.322Å in our structure, longer than the related Hg-Cl distance 2.284(5)Å in Thiele et al's report and the distances of mercury atoms to central chlorine atoms are 2.982(2) and 3.012(2)Å, respectively, shorter than the related one in their report. We consider, here, that the central chlorine atoms hold $Hg_6Cl_{13}^-$ aggregate tighter in our structure than that in Thiele's report.

Chapter 3

Analysing The Full-Range Composition of The Double Salts of Mercuric Chloride with Another Chloride and The Resultant Stoichiometries

3.1 Introduction

Stoichiometric evidence for new and interesting compounds had to be obtained by chemical analyses. At the end of last century and very early in this century, scientists had begun to study the double salts of mercuric chloride with another chloride salt and realized that there must be some relations between the composition of the mixtures and the formation of the double salts [36, 37, 38]. They invented the solubility method and used it to investigate a few mercuric chloride and the alkali chloride systems and obtained good results. These were carried out by gravimetric method—by precipitating mercuric(II) sulphide from the solution acidified with hydrochloric acid, filtering on a Gooch crucible, drying at 100°C and weighing the mercuric sulphide. According to their theories, a series of two or more results giving a constant composition of the residue and varying composition of the solution shows a pure double salt to be present, while constant solution composition and varying residue composition indicates a mixture of two salts. Also according to the ideas of Foote and Levy [36], the advantages of the method are that all double salts, forming at a given temperature, can be determined with a good degree of certainty and that the solubility conditions under which each salt forms are ascertained "Varying mixtures, carefully weighed, of mercuric chloride and an alkali chloride were treated with hot water enough to dissolve them, placed in the thermostat at 25°C and shaken, usually for several days" is the key part of the whole process. And also, carefully measuring the weight and volume of the solution aliquots are very important in order to obtain accurate results.

We have investigated several systems: $HgCl_2$+CsCl, $HgCl_2$+$[Co(NH_3)_6]Cl_3$, and $HgCl_2$+en·2HCl, and the results are given in Figures 1, 2 and 3. The graphs show the composition relationships of the mixtures. From the graphs, we can get the information about how many complexes can be formed in the full-range and what these complexes are. We have tried to make some pure compounds using the graphs we obtained, and analysed the crystals. For example, any mixture of CsCl and $HgCl_2$ in the range of 0.50-0.75g CsCl plus 2.00-1.75g $HgCl_2$ should crystalise the "**B**" material with composition $CsHg_3Cl_7$, corresponding to 18.0% CsCl. Some of the results coincided with what we expected from the graph, but some of the results did not. As part of our continuing investigations we prepared single crystals according to the graphs of en·2HCl + $HgCl_2$ and $Co(NH_3)_6Cl_3$ + $HgCl_2$ systems. The results are reported in the following chapters.

3.2 Experimental

The following 19 different weight ratio solutions (Table 3.1) were made, each using a total amount of 2.5 g of mixed solids. The volume of water used was adjusted to allow for the widely differing solubility of CsCl and $HgCl_2$.

Table 3.1

CsCl(g)	Wt%	$HgCl_2$(g)	Wt%	H_2O(ml)
0.125	5	2.375	95	15
0.250	10	2.250	90	15
0.375	15	2.125	85	15
0.500	20	2.000	80	15
0.625	25	1.875	75	15
0.750	30	1.750	70	10
0.875	35	1.625	65	10
1.000	40	1.500	60	10
1.125	45	1.375	55	10
1.250	50	1.250	50	10
1.375	55	1.125	45	10
1.500	60	1.000	40	10
1.625	65	0.875	35	10
1.750	70	0.750	30	10
1.875	75	0.625	25	10
2.000	80	0.500	20	5
2.215	85	0.375	15	5
2.250	90	0.250	10	5
2.375	95	0.125	5	5

The flasks containing the mixtures were attached to a Warburg apparatus (controlled temperature with shaking) and maintained at 45°C for about 24 hours. After this, the temperature was decreased to 25°C, at which it was held for another 24 hours. Then, each of the residual solutions was analysed for chloride and mercury. An sample calculation is given on page 32a. The results are shown in Figure 3.1. Constant

composition of the residues (vertical lines) shows a pure double salt and they are shown in A, B, C, D, E, F and G.

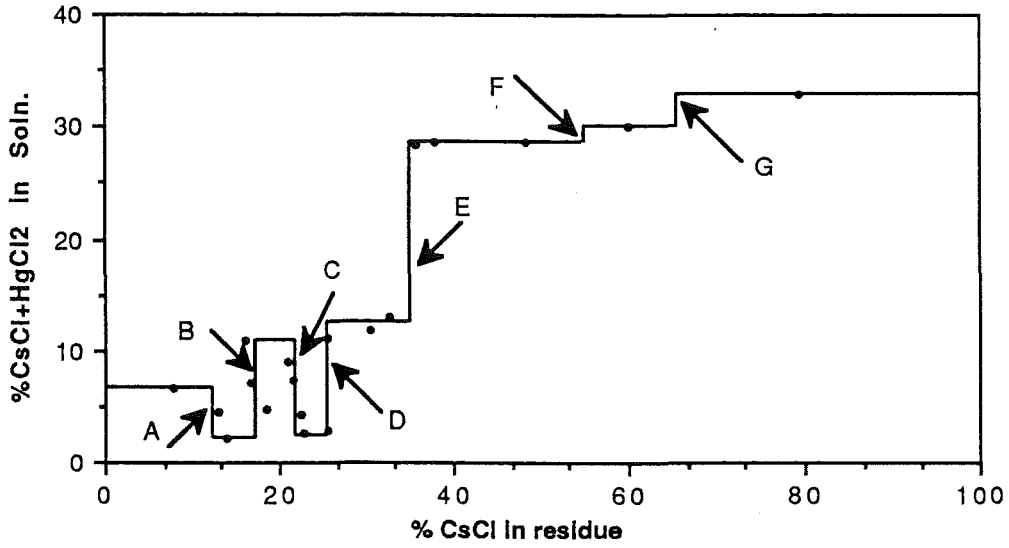


Figure 3.1 $CsCl+HgCl_2$

	Complex to be postulated	CsCl% (calc.)	CsCl% (found in this work)	CsCl% (found in Foote's work*)
A	$CsHg_5Cl_{11}$	11.1	16.5	11.1
B	$CsHg_3Cl_7$	17.1	18.0	--
C	$Cs_4Hg_9Cl_{22}$	21.6	21.5	--
D	$CsHg_2Cl_5$	23.7	24.0	23.5
E	$CsHgCl_3$	38.3	37.5	37.6
F	Cs_2HgCl_4	55.4	56.5	55.8
G	Cs_3HgCl_5	65.0	65.5	65.9

*: See reference 36.

3.3 Results and Discussion

3.3.1 Results

$[Co(NH_3)_6]Cl_3$+$HgCl_2$ system and en·2HCl+$HgCl_2$

The experimental procedures are the same as above. The results are shown in Figure 3.2 and Figure 3.3, and the pure double compounds are shown in A',B',C', D' (Figure.3.2) and A",B",C",D",E" (Figure.3.3).allow for the widely differing solubility of $[Co(NH_3)_6]Cl_3$ and $HgCl_2$.

The following 22 different weight ratio solutions (Table 3.2) were made, each using a total amount of 2.5 g of mixed solids. The volume of water used was adjusted to allow for the widely differing solubility of $[Co(NH_3)_6]Cl_3$ and $HgCl_2$.

Table 3.2

$[Co(NH_3)_6]Cl_3$(g)	Wt%	$HgCl_2$(g)	Wt%	H_2O(ml)
0.13	5	2.38	95	15
0.25	10	2.25	90	15
0.37	14.8	2.13	85.2	15
0.38	15.2	2.12	84.8	15
0.42	16.8	2.08	83.2	15
0.50	20	2.00	80	15
0.57	22.8	1.93	77.2	15
0.63	25	1.88	75	15
0.75	30	1.75	70	15
0.87	35	1.63	65	15
1.00	40	1.50	60	15
1.13	45	1.38	55	15
1.25	50	1.25	50	15
1.38	55	1.13	45	15
1.50	60	1.00	40	15
1.63	65	0.88	35	15
1.75	70	0.75	30	15
1.87	75	0.63	25	15
2.00	80	0.50	20	15
2.13	85	0.38	15	15
2.25	90	0.25	10	15
2.38	95	0.13	5	15

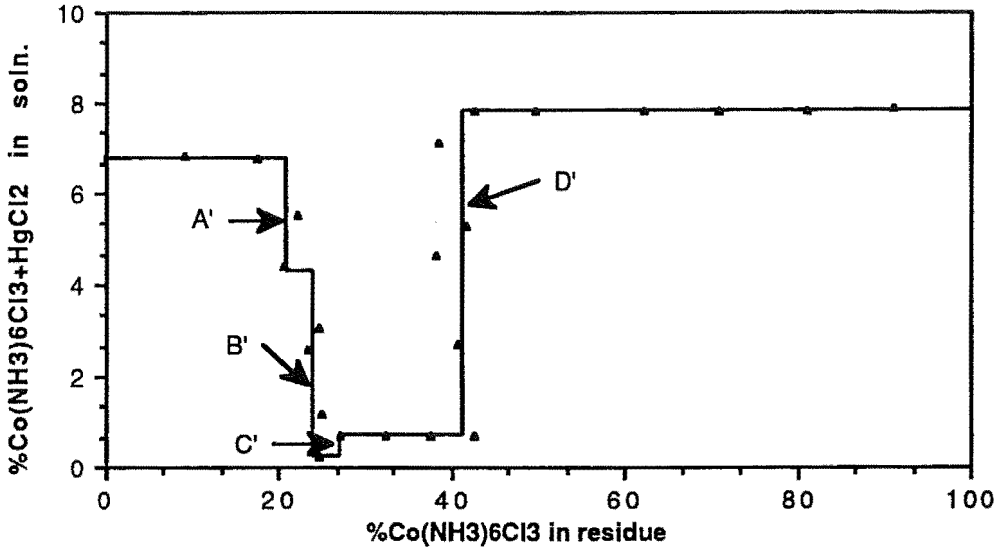


Figure 3.2 $[Co(NH_3)_6]Cl_3$+$HgCl_2$

	Complex to be postulated	$[Co(NH_3)_6]Cl_3$% (calc.)	$[Co(NH_3)_6]Cl_3$% (found)	Reference *
A'	$[Co(NH_3)_6][Hg_4Cl_{11}]$	19.8	20.0	--
B'	$[Co(NH_3)_6][HgCl_3]_3$#	24.7(24.3)	23.8	--
C'	$[Co(NH_3)_6]_2[Hg_5Cl_{11}]Cl_2$	28.3	27.5	--
X	$[Co(NH_3)_6][Hg_2Cl_7]$	33.0	--	[39]
D'	$[Co(NH_3)_6]_2[HgCl_4]_3$	39.6	41.0	--
Y	$[Co(NH_3)_6][HgCl_5]$&	49.6	--	[39]

*: This complex was reported in this reference, but we did not find them in our work.

#: Found to be $[Co(NH_3)_6][HgCl_3]_3 \cdot H_2O$ by X-ray single crystal structure analysis.

&: The single crystal structure for this complex has been determined [39].

The following 20 different weight ratio solutions (Table 3.3) were made, each using a total amount of 2.5 g of mixed solids (except No. 12). The volume of water used was adjusted to allow for the widely differing solubility of en·2HCl and $HgCl_2$.

Table 3.3

en·2HCl(g)	Wt%	$HgCl_2$(g)	Wt%	H_2O(ml)
0.13	5	2.38	95	7
0.25	10	2.25	90	7
0.38	15.2	2.12	84.8	7
0.50	20	2.00	80	7
0.63	25	1.88	75	7
0.75	30	1.75	70	7
0.87	35	1.63	65	7
1.00	40	1.50	60	7
1.13	45	1.38	55	7
1.25	50	1.25	50	7
1.38	55	1.13	45	7
3.00	60	2.00	40	7*
1.63	65	0.88	35	7
1.75	70	0.75	30	7
1.87	75	0.63	25	7
2.00	80	0.50	20	7
2.13	85	0.38	15	7
2.25	90	0.25	10	7
2.38	95	0.13	5	7
5.00	100	0.00	0	10

*: Additional 1.50g of en·2HCl and 1.00g of $HgCl_2$ were added as there were no crystals at 25°C when 2.5g of total amount of solids were used.

The experimental procedures to determine the compositions of each solution and residue are shown in full for the seventh entry in table 3.3.

0.87g of en·2HCl and 1.63g of $HgCl_2$ were accurately weighed and mixed in a 25ml of flask with 7.0ml of water. The sample flask was attached to a Warburg apparatus (controlled temperature with shaking) and maintained at 45°C for ~24 hours to dislove all the solids, the temperature was then decreased to 25°C for another ~24 hours to let the compounds crystallize.

For chloride analysis, two drops of the solution (0.10g, accurately weighed) were placed into a 50ml flask and diluted to 25ml with distilled water, then 2ml of 0.1M $HClO_4$ solution was added to acidify the sample. The solution was then titrated with standard $Hg(NO_3)_2$ solution (9.45×10^{-3}M).

The volume of $Hg(NO_3)_2$ used: (23.10 - 16.60)ml = 6.50ml
so, M_{Cl^-} in 0.10g of oringinal solution:
$2 \times 6.50 \times 10^{-3} \times 9.45 \times 10^{-3} = 1.228 \times 10^{-4}$ (mol)
en·2HCl in 100g of solution:
$1.228/2 \times 10^{-4} \times 133.02 \times 10^{3} = 8.17$g/100g soln. as: en·2HCl $\rightarrow 2Cl^-$

A second of two drops of solution (0.10g, accurately weighed) in another clean 50ml flask were used for Hg^{2+} ($HgCl_2$) analysis. As in the first sample, the solution was diluted into 25ml with distilled water, then 2ml of buffer (NH_3/NH_4Cl, ca,pH=10) and 10.00ml of standard EDTA (0.0096M) were added to the solution, which was shaken thoroughly. The solution was then"back titrated" with standard $ZnSO_4$ solution (0.010M).

V_{ZnSO_4} = (44.52-38.80)ml = 5.72ml, V_{EDTA}=10.00ml
M_{EDTA} = 0.0096M, M_{ZnSO_4} = 0.0100M
$M_{HgCl_2} = (0.0096 \times 10.00 \times 10^{-3} - 5.72 \times 0.0100 \times 10^{-3}) = 3.88 \times 10^{-5}$ (mol)
$HgCl_2$ in 100g of solution:
$3.88 \times 10^{-5} \times 10^{3} \times 271.52 = 10.56$ g/100g soln.

After the analyses, 1.0ml of the original solution was weighed to measure the density.

D = 1.13g/ml

Finally the composition of the residue was calculated as follows:

residue in en·2HCl = [0.87 - (7.00x1.13x8.17/100)]g = (0.87 - 0.66)g = 0.22g
residue in $HgCl_2$ = [1.63 - (7.00x1.13x10.56/100)= (1.63 - 0.81)g = 0.82g

so, $\varepsilon^* = 10.56 + 8.17 = 18.73$ (g/100g soln)

ε^*: The total amount of en·2HCl + $HgCl_2$ in 100g of solution, ie, % of en·2HCl + $HgCl_2$ in soln.

Using the following error estimates:

each weighing	±0.005g
each titration volume	±0.1ml
pipette volume	±0.5%
standard solution	±1%

ε has an uncertainity of ±10.79%, ie, $\varepsilon = (18.73 + 2.02)\%$

and the % en·2HCl in residue has an uncertainity of ±5.15%, ie,

% en·2HCl in residue = (0.22 + 0.02)g

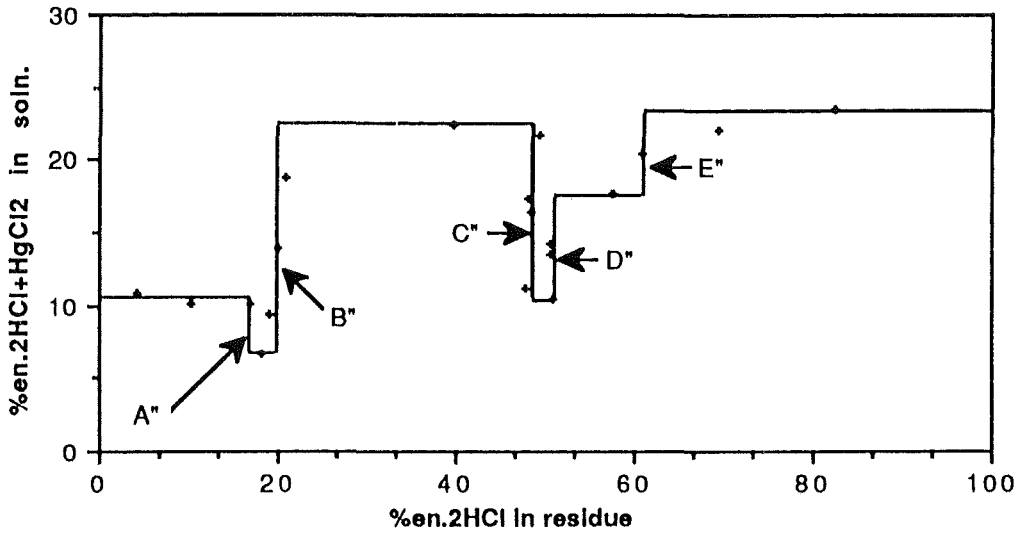


Figure 3.3 en·2HCl+$HgCl_2$

	Complex to be postulated	en·2HCl% (calc.)	en·2HCl% (found)
A"	$[H_2en]_2[Hg_5Cl_{14}]^{\#}$	16.4	16.5
B"	$[H_2en][HgCl_3]_2$	19.7	20.0
X	$[H_2en][HgCl_4]$	32.8	--*
C"	$[H_2en]_2\cdot[HgCl_4]\cdot 2Cl$	49.5	48.5
D"	$[H_2en]_7[Hg_3Cl_{20}]\cdot 4H_2O^{\#}$	51.2	51.5
E"	$[H_2en]_3\cdot[HgCl_4]\cdot 4Cl$	59.5	60.5

*: According to the properties of $HgCl_2$, we think this complex should be formed, but we did not find it.

#: The stoichiometries of these two compounds fit the experimental results however we have not proved them yet.

3.3.2 Discussion

We prepared the $CsCl+HgCl_2$ system first and compared our results with those obtained by Foote and Levy before. We used a different analytical method from theirs. As we mentioned before, they used gravimetric methods in their work. In our experiments, the analyses were carried out by back-titrating unreacted standard EDTA with standard $ZnSO_4$ solutions for Hg^{2+} determination, and titrating Cl^- using standard Hg^{2+} solutions for Cl^- determination. We used this method to analyse $CsCl+HgCl_2$ and $en{\cdot}2HCl+HgCl_2$ systems and obtained reasonable results. However we had to use both back-titration and visible absorption spectrometry to determine the compositions of the solutions from the $HgCl_2+[Co(NH_3)_6]Cl_3$ system because of the strong orange color of the Co(III) ions. Compared to the gravimetric method used by Foote and Levy, the back-titration we used in our analyses has the advantages of being faster, simpler and easier to carry out, however it is not always easy to use back-titration. For example, when the concentration of a solution gets very high, the volume of the solution could be very different from the weight of the solution. In this condition, we had to measure accurately both volume and weight of a solution to obtain accurate results during our analyses. Often problems for this method are, (i) These are equilibrium compositions at 25°C, and metastable compositions will not be detected; (ii) Compounds that crystallise with H_2O of crystallization are difficult to fit into the analytical composition ranges as we can not detect the amount of crystallization H_2O molecules by our analytical methods. Nevertheless, we still consider the "Full-range solubility method" is an effective way to obtain the total information about formation of a double salts of mercuric(II) chloride with another chloride.

Chapter 4

Preparation and X-ray Crystal Structure Determination of Two Chloromercury(II) Salts: $[NH_3(CH_2)_2NH_3][HgCl_4][Cl]_2$ and $[NH_3(CH_2)_2NH_3][Hg_2Cl_6]$

4.1 Introduction

Salts containing chloromercury(II) anions exhibit a wide range of stoichiometric forms. For example: mononuclear, e.g. $HgCl_4^{2-}$ [40] and polynuclear, e.g. $Hg_6Cl_{13}^-$ [35]. There are also numerous examples of chain structures [41, 42, 43]. However the nature of the anionic groups within the lattice is not distinguishable without single crystal X-ray structure analysis. The full-range solubility of mercury(II) chloride $HgCl_2$ with ethylenediammonium hydrochloride $[H_2en]\cdot[Cl]_2$ has been outlined in Chapter 3 and the two salts with the analytical compositions $[H_2en][HgCl_3]_2$ (1) and $[H_2en]_2[HgCl_6]$ (2) have been prepared and studied using X-ray single crystal structure analysis as part of our continuing investigations on the structural complexity of chloromercury(II) anions [44, 45]. Here in this chapter we report the X-ray structure analysis results for the two 1,2-ethanediammonium chloromercury(II) salts.

4.2 Experimental

4.2.1 Crystal preparations

Following the solubility graph of $[H_2en]\cdot[Cl]_2$ with $HgCl_2$ (chapter 3), we tried to make crystals at the vertical lines B" and C". From the mole ratio, we postulated that the crystals should be $[H_2en]_2[HgCl_6]$ (B") and $[H_2en][Hg_2Cl_6]$ (C") respectively. B" was made by separately dissolving $[H_2en][Cl]_2$ (0.8g, 6.0mmol) and $HgCl_2$ (1.7g, 6.3mmol) in 50 ml of hot water then mixing the two solutions together then cooling. On standing at room temperature for a few days, colourless, triclinic crystals deposited. There was only one kind of crystal formed.

$[H_2en][Cl]_2$ 1.25g (9.4mmol) and $HgCl_2$ 1.25g (4.6mmol) were separately dissolved in ~50ml of hot water and then the solutions were mixed together. With a similar procedure, colourless, orthorhombic crystals, C", were obtained. We also checked these crystals to make sure only one form existed.

The two reactions are:

$$2[H_2en][Cl_2] + HgCl_2 \rightarrow [H_2en]_2[HgCl_4][Cl]_2 \quad (C")$$

$$[H_2en][Cl_2] + 2HgCl_2 \rightarrow [H_2en][Hg_2Cl_6] \quad (B")$$

4.2.2 X-ray Crystal Determinations

Crystal data for the two compounds are listed in Table 4.1. Intensity data for the two chloromercury(II) salts were collected at 153K with a Nicolet R3m four-circle diffractometer. Graphite monochromated MoKα radiation (λ=0.71069Å) was used with fixed speed omega scans.

The structures were solved by conventional Patterson and Fourier methods and refined by blocked-cascade least-squares procedures. The mercury and chlorine atoms were refined with anisotropic thermal parameters but nitrogen and carbon were refined isotropically. The hydrogen atoms were inserted at calculated positions using a riding model with the thermal parameters fixed at 0.05. The final difference Fourier maps show that the largest difference peaks are 3.09eÅ^{-3} (**1**) and 1.23eÅ^{-3} (**2**) and the largest difference holes are -6.09eÅ^{-3} (**1**) and -1.71eÅ^{-3} (**2**). They lie close to the mercury atoms. Atomic coordinates for non-hydrogen atoms, bond lengths and bond angles for both of the structures are listed in Tables 4.2-4.7.

Table 4.1 Crystal Data

Complex	$[H_2en][Hg_2Cl_6]$ (1)	$[H_2en]_2[HgCl_4][Cl]_2$ (2)
Molecular Formula	$C_2H_{10}N_2Cl_6Hg_2$	$C_4H_{20}N_4Cl_6Hg$
Formula Weight	676.01	537.54
Crystal Size(mm)	0.52x0.12x0.11	0.40x0.30x0.20
Cell Lattice	triclinic	orthorhombic
Space Group	$P\bar{1}$	Pnma
a(Å)	6.128(1)	12.759(4)
b(Å)	6.984(1)	6.073(20
c(Å)	8.045(2)	19.829(7)
α(°)	77.81(2)	90.0
β(°)	85.87(2)	90.0
γ(°)	66.40(2)	90.0
V(Å)^3	616.7(2)	1536.5(9)
Z	2	4
Dcalc(g/cc)	3.64	2.32
Temperature(K)	153	153
F(000)	298	1016
Linear absorption coefficient(cm^{-1})	261.32	110.50
Transmission factors	0.092	0.328
	0.137	0.970
Merge	0.0440	0.0300
Scan Mode	ω	ω
Octants	0,-k,-l	0,0,0
	h,k,l	h,k,l
2θmax(°)	50	52
Reflections measured	2432	1793
Reflections used	1082	1053
Parameters refined	45	54
Weighting(gx10^3)	8.58	1.54
GOOF	0.66	0.57
R	5.24	3.67
R_w	5.44	3.66

for $[H_2en]_2[HgCl_4][Cl]_2$

Table 4.2 Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2 x10^3$)

	x	y	z	U(eq)
Hg(1)	1945(1)	1748(1)	2500	16(1)
Cl(1)	3964(3)	1874(8)	2500	22(1)
Cl(2)	1748(3)	-2871(6)	2500	16(1)
Cl(3)	1495(2)	2097(4)	3668(1)	18(1)
Cl(4)	4030(2)	2149(4)	4906(1)	14(1)
N(1)	5008(8)	1363(16)	6392(5)	20(2)
N(2)	6598(7)	2881(14)	5286(4)	12(2)
C(1)	5735(9)	3229(20)	6422(5)	18(2)
C(2)	6748(8)	2906(18)	6035(5)	13(2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 4.3 Bond lengths (Å)

Hg(1)-Cl(1)	2.576 (4)	Hg(1)-Cl(2)	2.816 (4)
Hg(1)-Cl(3)	2.395 (3)	Hg(1)-Cl(3A)	2.395 (3)
N(1)-C(1)	1.466 (15)	N(2)-C(2)	1.497 (13)
C(1)-C(2)	1.516 (15)		

Table 4.4 Bond angles (°)

Cl(1)-Hg(1)-Cl(2)	96.8(1)	Cl(1)-Hg(1)-Cl(3)	103.7(1)
Cl(2)-Hg(1)-Cl(3)	93.8(1)	Cl(1)-Hg(1)-Cl(3A)	103.7(1)
Cl(2)-Hg(1)-Cl(3A)	93.8(1)	Cl(3)-Hg(1)-Cl(3A)	150.4(1)
N(1)-C(1)-C(2)	114.8(9)	N(2)-C(2)-C(1)	113.3(8)

for $[H_2en][Hg_2Cl_6]$

Table 4.5 Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2x10^3$)

	x	y	z	U(eq)
Hg(1)	1723(1)	2048(1)	4343(1)	10(1)
Cl(1)	597(7)	2925(6)	7025(5)	13(1)
Cl(2)	1815(6)	1767(6)	1469(4)	10(1)
Cl(3)	3821(7)	-2287(6)	5531(5)	10(1)
N(1)	4762(20)	6642(19)	1649(15)	8(2)
C(1)	4028(24)	6028(22)	168(19)	10(3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 4.6 Bond lengths (Å)

Hg(1)-Cl(1)	2.348 (4)	Hg(1)-Cl(2)	2.356 (4)
Hg(1)-Cl(3)	2.752 (3)	Hg(1)-Cl(3A)	2.812 (4)
Cl(3)-Hg(1A)	2.812 (4)	N(1)-C(1)	1.501 (23)
C(1)-C(1A)	1.517 (26)		

Table 4.7 Bond angles (°)

Cl(1)-Hg(1)-Cl(2)	165.1(1)	Cl(1)-Hg(1)-Cl(3)	95.6(1)
Cl(2)-Hg(1)-Cl(3)	94.3(1)	Cl(1)-Hg(1)-Cl(3A)	93.7(1)
Cl(2)-Hg(1)-Cl(3A)	97.5(1)	Cl(3)-Hg(1)-Cl(3A)	89.7(1)
Hg(1)-Cl(3)-Hg(1A)	90.3(1)	N(1)-C(1)-C(1A)	109.2(15)

4.3 Results and Structure Description

The two ethylenediammonium chloromercurate(II) salts have been shown to be $[H_2en^{2+}][Hg_2Cl_6^{2-}]$ (triclinic) and $[H_2en^{2+}]_2[HgCl_4^{2-}][Cl^-]_2$ (orthorhombic) by the X-ray crystal structure analyses which were carried out to establish the nature of their chloromercury(II) anions.

4.3.1 The Ethylenediammonium Cations

The ethylenediammonium cation can adopt either the *gauche* or *trans* configuration (Figure 4.1). In the $[H_2en^{2+}][Hg_2Cl_6^{2-}]$ salt, the configuration of the cation is *trans* with N-C-C-N=180° and in the $[H_2en^{2+}]_2[HgCl_4^{2-}][Cl^-]_2$ salt, the configuration is *gauche* with a dihedral angle of 69.2°, similar to that of 72.5° in the $[H_2en^{2+}][CoCl_4^{2-}][Cl^-]_2$ [46] and 71.4° in the $[H_2en^{2+}][citrate^{2-}]$ [47].

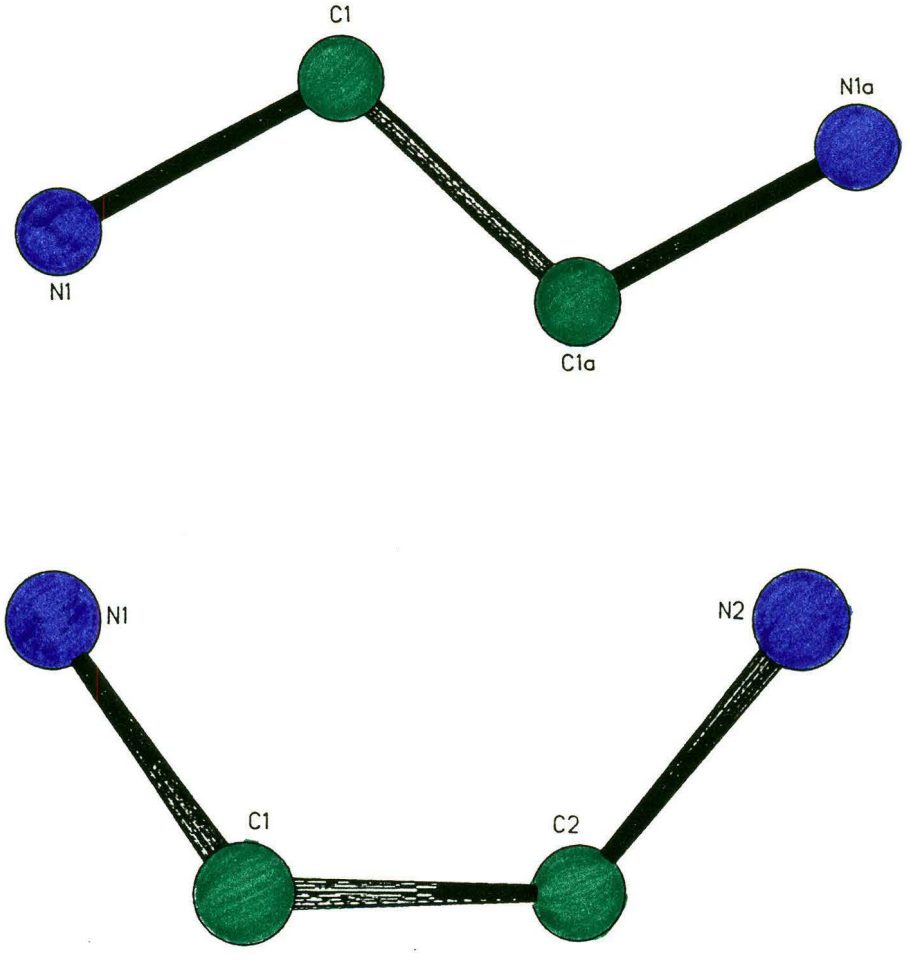


Figure 4.1 The *trans* and *gauche* configuration of the ethylenediammoniam cation

4.3.2 The $Hg_xCl_y^{n-}$ Anions

The $Hg_2Cl_6^{2-}$ Anion in $[H_2en][Hg_2Cl_6]$

This structure consists of $[Hg_2Cl_6^{2-}]$ complex anions with isolated $[H_2en^{2+}]$ counter cations. Each of these ions contains an internal crystallographic centre of symmetry. There are many chloromercury(II) salts which contain anions of the empirical stoichiometry $HgCl_3^-$. They can exist as discrete monomeric $HgCl_3^-$ units[40], $(HgCl_3^-)_n$ chain structures[48], $Hg_2Cl_6^{2-}$ dimeric edge-shared bitetrahedra[49, 50] or $(Hg_3Cl_9^{3-})_n$ chains[51].

In $[H_2en^{2+}][HgCl_3^-]_2$ the chloromercurate(II) anion is found to adopt the centrosymmetric $Hg_2Cl_6^{2-}$ arrangement with a terminal Cl-Hg-Cl angle of 165.1(1)° (Figure 4.2).

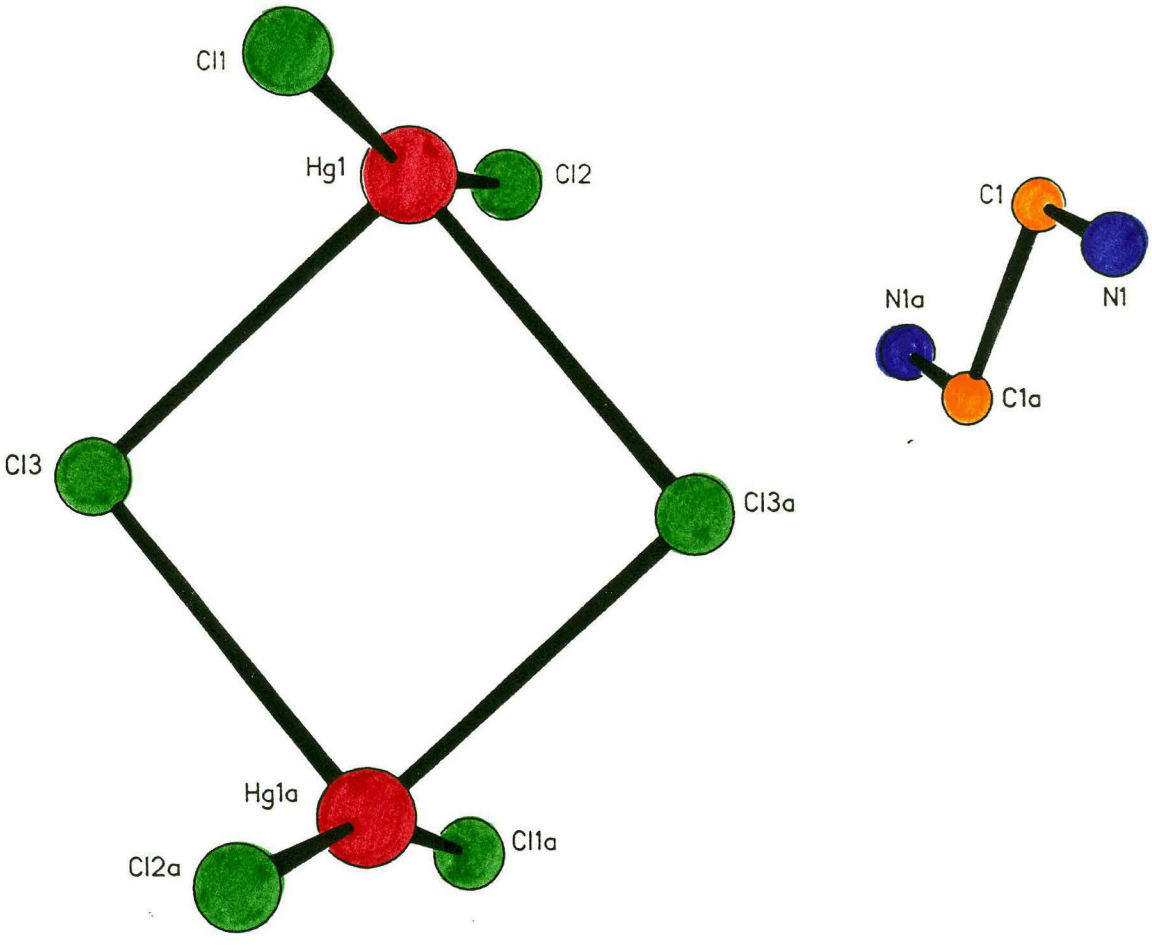


Figure 4.2 The molecular structure of $[H_2en][Hg_2Cl_6]$

It appears to be a distorted edge-shared bitetrahedron, similar to that reported by Larock, et al[40], with its center of mass coincident with a crystallographic center of symmetry. The two independent Hg-Cl bridging distances at 2.751(3) and 2.811(5)Å lead to a slightly asymmetric bridging system which has been found in most structures containing the $Hg_2Cl_6^{2-}$ moiety (Table 4.8). In this anion, the two terminal Hg-Cl bond lengths are quite short [Hg(1)-Cl(1) 2.349(1)Å and Hg(1)-Cl(2) 2.353(1)Å] with a Cl(1)-Hg(1)-Cl(2) angle of 165.1(1)°. The packing diagram of $[H_2en][Hg_2Cl_6]$ is shown in Figure 4.3.

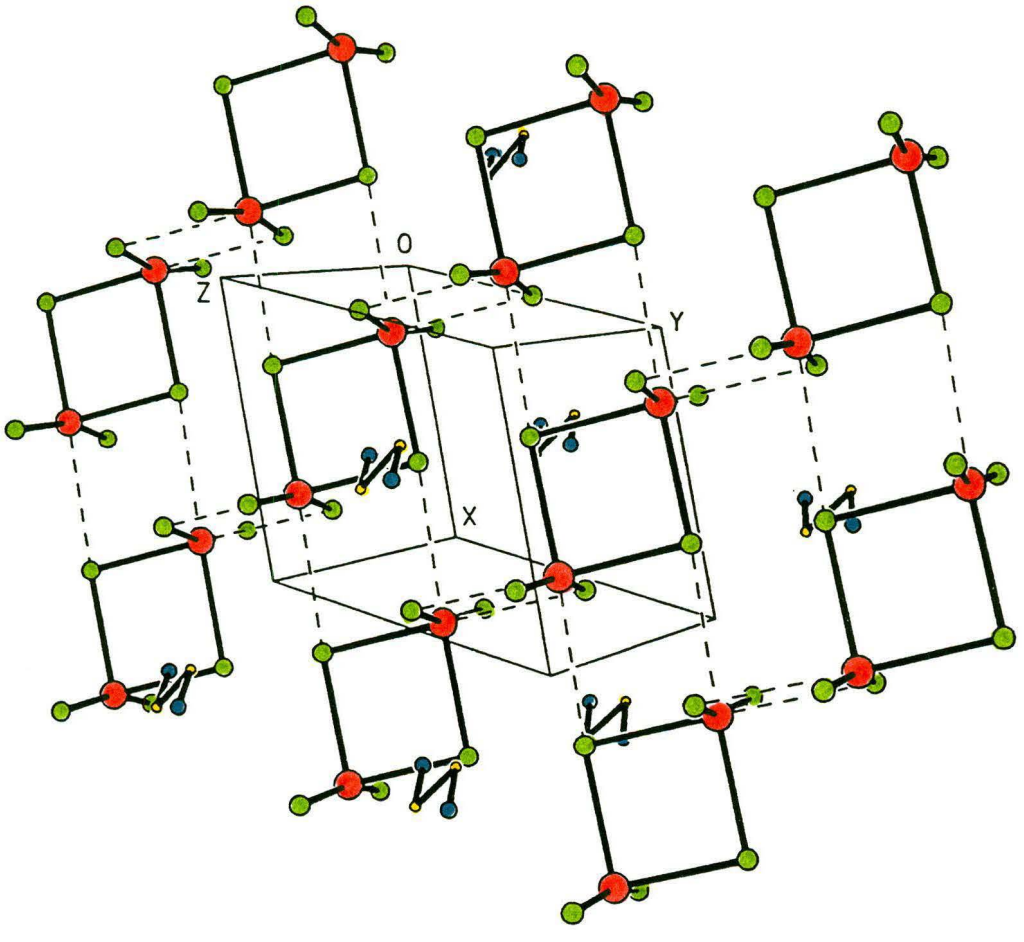


Figure 4.3 The packing diagram of $[H_2en][Hg_2Cl_6]$

We can see that $[Hg_2Cl_6^{2-}]$ does not exist as discrete units, as is found in many other cases (Table 8.4) but rather as a polymeric chain structure. The intermolecular distances Hg(1)···Cl(1) and Hg(1)···Cl(3) are 3.18 and 3.33Å, respectively. Though the Hg(1)···Cl(3) distance 3.33Å is rather long for Hg-Cl interaction we still consider it as an effective coordination within the three dimensional network of $[Hg_2Cl_6^{2-}]$ anionic polyhedra. The counter cations, $[H_2en^{2+}]$ reside in the cavities between them. We consider, here, that the effective coordination number for the mercury(II) atom is six. Compared with the $Hg_2Cl_6^{2-}$ anions which are described above, the terminal Cl-Hg-Cl angle of 165.1° is towards the more "open" end of the range observed(119-167°) (Table 4.8). The wide range of the terminal angle exemplifies the considerable degree of flexibility which exists in the $Hg_2Cl_6^{2-}$ anion. There may be an approximate correlation between the Hg-Cl (terminal) length and the terminal Cl-Hg-Cl angle for $Hg_2Cl_6^{2-}$ anions. However, why $HgCl_3^-$ can have such different arrangements and which factors control the formation of any particular $(HgCl_3^-)_n$ arrangement are still unidentified.

The $HgCl_4^{2-}$ in $[H_2en]_2[HgCl_4][Cl]_2$

We thought that the salt $[H_2en]_2[HgCl_6]$ would contain the $HgCl_6^{4-}$ anion but it turned out that it was not the case. Two isolated chloride ions were found for each Hg atom, so the salt is best represented by the formal stoichiometry of $[H_2en]_2[HgCl_4][Cl]_2$. The structure consists of $[HgCl_4^{2-}]$ complex anions and two isolated chloride ions Cl^- with two isolated $[H_2en^{2+}]$ counter cations (Figure 4.4). However, the $HgCl_4^{2-}$ units are not isolated in this structure, as they are in many other structures [23, 54, 55], but are linked into chains and each Hg atom is 5 coordinate with a fifth Hg-Cl distance of 3.28Å (Figure 4.5).

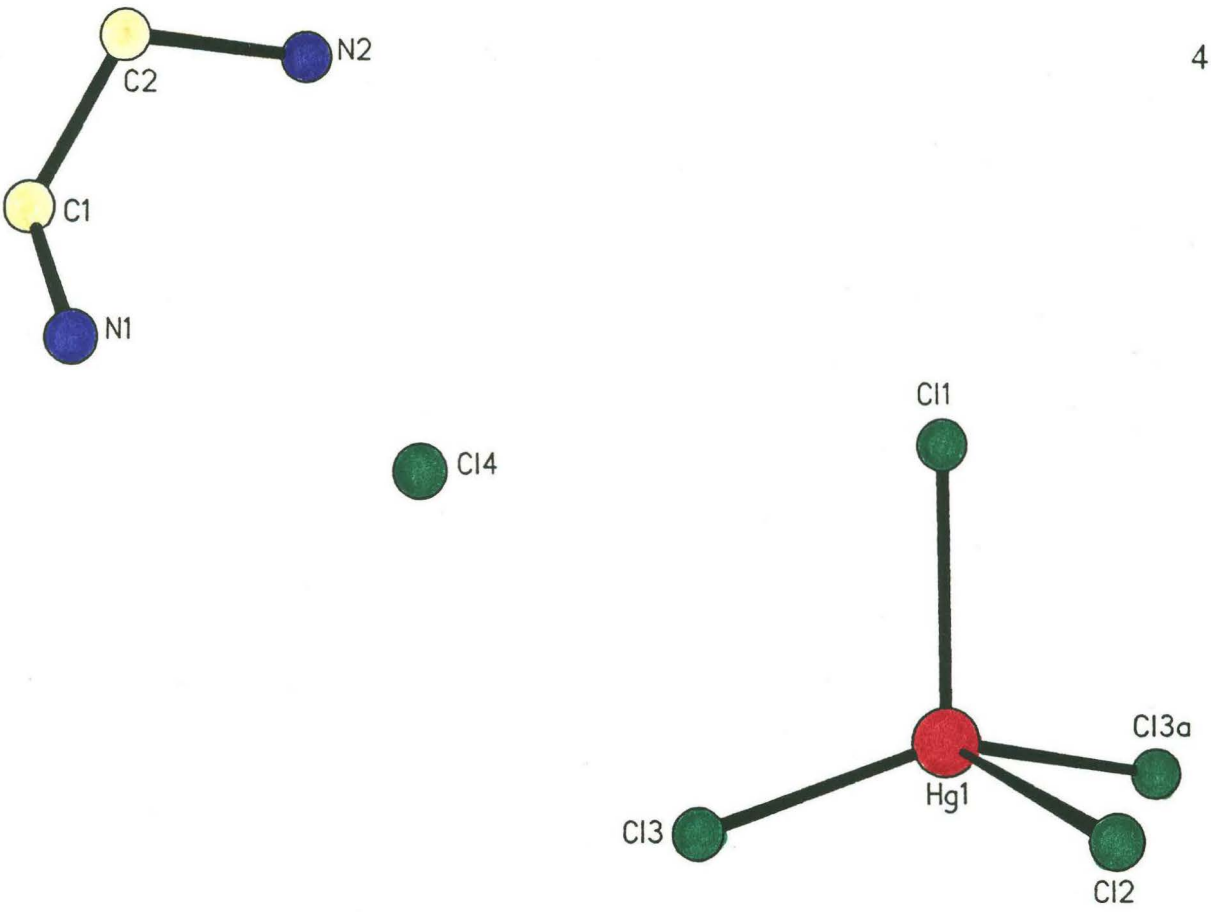


Figure 4.4 The molecular structure of $[H_2en]_2[HgCl_4][Cl]_2$

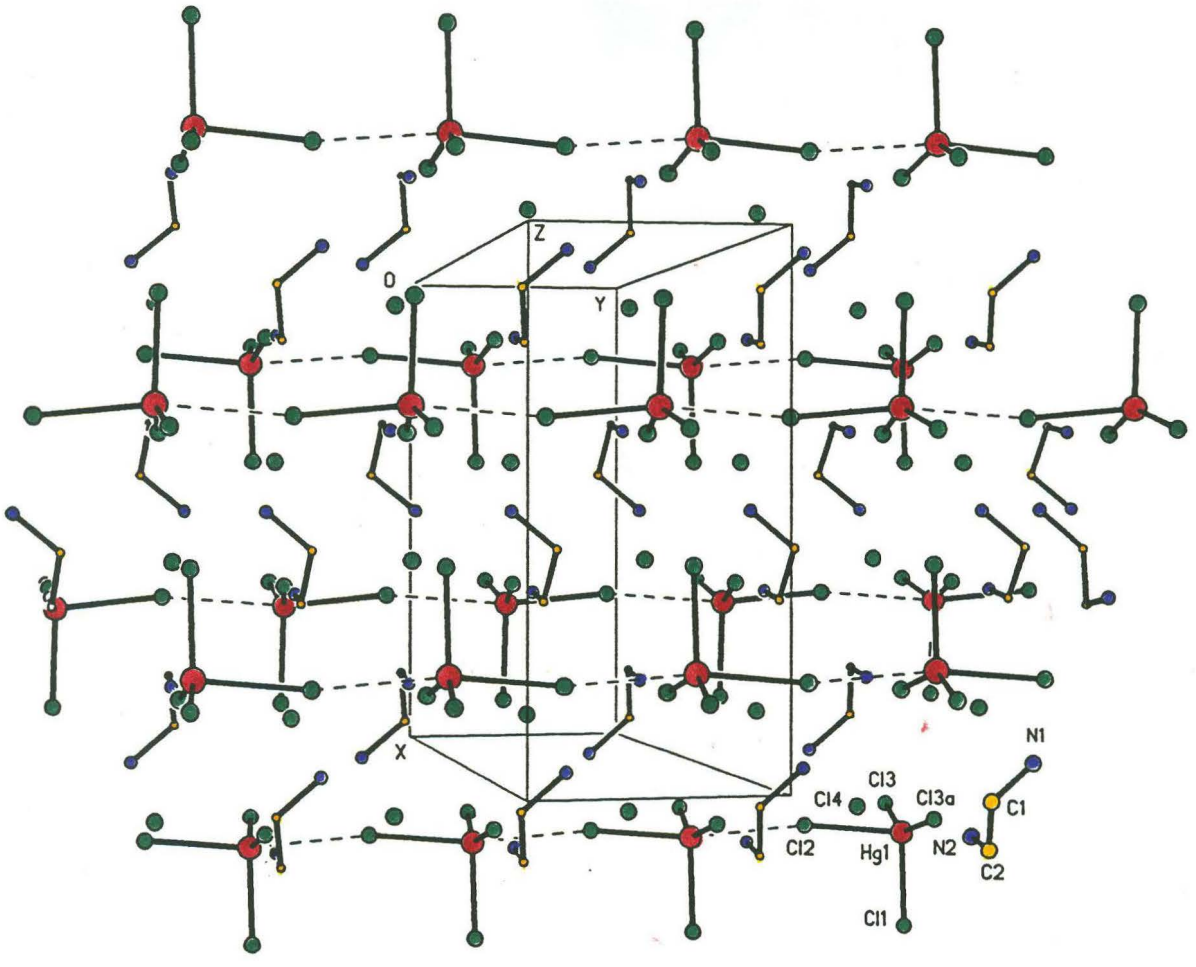


Figure 4.5 The packing diagram of $[H_2en]_2[HgCl_4][Cl]_2$

Even though this distance is very long for Hg-Cl interaction (the sum of the van der Waals radii for Hg-Cl is 3.35Å), very large deviations from idealized tetrahedral geometry are evident at the center of the $HgCl_4^{2-}$ units.

The geometry of the $HgCl_4^{2-}$ anion in the structure $[H_2en]_2[HgCl_4][Cl]_2$ is roughly tetrahedral with two short Hg-Cl bonds of 2.395(3)Å and two long Hg-Cl bonds of 2.576(4) and 2.816(4)Å and the fifth long contact 3.28Å. For more or less isolated pseudo-tetrahedral $HgCl_4^{2-}$ ions, e.g. in $[DABCO^{2+}][HgCl_4^{2-}]\cdot H_2O$ [56], the Cl-Hg-Cl angles vary from 100.5 to 121.1°, but in the present chain structure, the anion exhibits a more irregular geometry with the Cl-Hg-Cl angles varying from 93.8 to 150.2°. $[HgCl_4^{2-}]$ tetrahedra have been found in a number of crystal structures, such as: $[CH_3NH_3]_2HgCl_4$ and $[(CH_3)_4N]_2HgCl_4$ [54] etc. All these structures deviated from ideal tetrahedra to different degrees, indicating that the $[HgCl_4^{2-}]$ group is easily distorted by crystal packing effects. Ferguson, et al [57] and Mason, et al [58] have reported an example in which the same anion $[HgCl_4^{2-}]$ exhibits a much more regular geometry with bond distance ranges of 2.48-2.51Å and bond angle ranges of 98-119°, respectively. However Larock, et al's [40] previous report of an $[HgCl_4^{2-}]$ anion is much more in agreement with our results. In their structure $(ClHgNC_6H_{12}Cl)_2HgCl_4(C_6H_6)\cdot H_2O$ they observed that the bond distances for $[HgCl_4^{2-}]$ anion are 2.387(5) and 2.643(4)Å, respectively and the bond angles range from 96.5-141.1°. But once again there are some significant differences between these two $[HgCl_4^{2-}]$ anions. In Larock's report, $[HgCl_4^{2-}]$ anions link to the Hg(2) in the counter cations through chloride ions [Cl(1) and Cl(2)] at the distances of Cl(1)-Hg(2) 3.06 and 3.36Å, Cl(2)-Hg(2) 3.23Å. Thus the effective coordination number for Hg(1) in the $[HgCl_4^{2-}]$ anion is four. However in our case $[HgCl_4^{2-}]$ anions link together into a chain through the fifth long contact Hg(1)-Cl(2) 3.28Å. So we consider that the effective coordination number for mercury(II) is five.

A wide spectrum of $HgCl_4^{2-}$ interactions is now developing, varying from isolated pseudo-tetrahedral units through weakly attracted close contacts to distinct chain development. The chain structures can be modified by the close association of two $HgCl_4^{2-}$ units (as found in $[H_4trien^{4+}][Hg_2Cl_8^{4-}]$) or by branching to give edge-shared arrangements.

Chapter 5

Preparation and X-ray Crystal Structure Determination of $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$ and *trans*-$[CoCl_2(en)_2]_2[Hg_2Cl_6]$

5.1 Introduction

In chapter 3, we discussed the analytical results of the full-range composition for both en·2HCl + $HgCl_2$ and $[Co(NH_3)_6]Cl_3$ + $HgCl_2$ systems. We prepared some of the postulated compounds [B" and C" (see chapter 3)] for the en·2HCl + $HgCl_2$ system and determined their structures and reported the results in chapter 4. According to our analytical results for $[Co(NH_3)_6]Cl_3$ + $HgCl_2$ system, we again prepared the postulated compounds (B' and D') but obtained only $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$ (B') . As part of our continuing investigations on salts containing chloromercury(II) anions, we studied the structures of two cobalt(III) complexes where the empirical formula suggest the formation of the $(HgCl_3^-)_n$ anion, viz. $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$ and *trans*-$[CoCl_2(en)_2][HgCl_3]$. However, as we have previously found, formal stoichiometry rarely reflects the nature of the chloromercury(II) anion in the crystal lattice [40, 44, 45], and these salts are no exception. In the former, a unique $(Hg_3Cl_9^{3-})_n$ chain is developed and in the latter, the $HgCl_3^-$ anion has dimerised to form the well known $Hg_2Cl_6^{2-}$ unit.

5.2 Experimental

5.2.1 Preparation of Single Crystals

$[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$

Using quantities calculated from our previous results, 0.25g of $[Co(NH_3)_6]Cl_3$ and 1.00g of $HgCl_2$ were separately dissolved in 100mL of hot water, the solutions were mixed and left to stand in an open beaker. Orange, needle and suitable crystals for X-ray structure analysis deposited

after a few days at room temperature. X-ray single crystal structure analysis proved that the crystals were the postulated $[Co(NH_3)_6][Hg_3Cl_9]$ compound with a crystallization water molecule–$[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$. We also tried to prepare another postulated compound $[Co(NH_3)_6]_2\cdot[HgCl_4]_3$ (D') with a similar procedure by using 1.50g of $Co(NH_3)_6Cl_3$ and 1.00g of $HgCl_2$. However, the crystals obtained from the solution were shown by X-ray single crystal structure analysis, to be the same as the first crystals.

Also in the presence of excess of HCl, other salts such as $[Co(NH_3)_6][HgCl_5]$ [28, 39] and $[Co(NH_3)_6][Hg_2Cl_7]$ [39] can be obtained.

***trans*-$[CoCl_2(en)_2]_2[Hg_2Cl_6]$**

Beautiful, regular, green crystals of *trans*-$[CoCl_2(en)_2]_2[Hg_2Cl_6]$ of suitable for X-ray single crystal structure analysis deposit rather quickly when *trans*-$[CoCl_2(en)_2]Cl\cdot HCl\cdot 2H_2O$ (1g) in 3M HCl (50mL, room temperature) is added to $HgCl_2$ (3g) in 3M HCl (50mL, 60°C).

5.2.2 Structure determinations

Crystal data for these two chloro-mercury(II) salts are listed in Table 5.1.

The structures were solved by conventional Patterson and Fourier methods and refined by blocked cascade least-squares procedures. For structure $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$ (**1**), only Hg, Co, Cl and O atoms were refined with anisotropic thermal parameters, but for structure *trans*-$[CoCl_2(en)_2]_2[Hg_2Cl_6]$ (**2**) satisfactory refinement was obtained with anisotropic thermal parameters for all non-hydrogen atoms. For both structures (**1**) and (**2**), the appropriate C-H and N-H hydrogen atoms were included in their calculated positions. The highest peaks in the final difference map are $3.11eÅ^{-3}$ (**1**) and $0.93eÅ^{-3}$ (**2**) and the largest holes are $-1.75eÅ^{-3}$ (**1**) and $-1.56eÅ^{-3}$ (**2**). These all lie close to the mercury(II) positions.

Tables 5.2 and 5.5 list the non-hydrogen atom coordinates for structures (**1**) and (**2**), respectively. Bond lengths and bond angles for these two compounds are listed in Tables 5.3, 5.4, 5.6 and 5.7.

Table 5.1. Crystal Data

Complex	$[Co(NH_3)_6][Hg_3Cl_9]H_2O$ (**1**)	*trans*-$[CoCl_2(en)_2]_2[Hg_2Cl_6]$ (**2**)
Molecular formula	$H_{20}N_6OCl_9CoHg_3$	$C_8H_{32}N_8Cl_{10}Co_2Hg_2$
Formula weight	1100.0	1114.0
Crystal size (mm)	0.50x0.22x0.15	0.28x0.28x0.26
Space group	monoclinic $P2_1/c$	monoclinic $P2_1/n$
a(Å)	7.943(2)	9.110(2)
b(Å)	21.070(9)	8.811(3)
c(Å)	12.413(4)	17.297(8)
β(°)	90.33(2)	90.86(4)
V(Å^3)	2077.4	1388.4
Z	4	2
D_{calc}(g/cc)	3.52	2.73
Temperature(K)	153	153
F(000)	1951	1040
Linear absorption coefficient (cm^{-1})	240.58	131.86
Transmission factors	0.537, 0.201	0.839, 0.467
Merge	0.062	0.024
Scan mode	ω	ω
Octants	h, k, ±l	h, k, ±l
2θmax(°)	52	52
Reflections measured	3922	2748
Reflections used	2480	1993
Parameters refined	146	136
Weighting (gx10^3)	1.31	2.00
GOOF	1.15	0.80
R	4.50	3.37
R_w	4.56	3.71

for $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$

Table 5.2 Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2 x10^3$)

	x	y	z	U(eq)
Hg(1)	1219(1)	1969(1)	4785(1)	19(1)
Hg(2)	967(1)	1187(1)	1306(1)	16(1)
Hg(3)	1381(1)	9771(1)	6285(1)	17(1)
Co(1)	-3825(3)	1281(1)	-1988(2)	10(1)
Cl(1)	865(7)	1657(2)	-630(3)	16(1)
Cl(2)	-1305(7)	422(2)	1249(4)	22(2)
Cl(3)	-1687(7)	1850(2)	4724(4)	18(1)
Cl(4)	3901(6)	740(2)	1112(4)	17(1)
Cl(5)	4110(6)	2069(2)	4966(4)	20(2)
Cl(6)	1176(7)	2151(2)	2348(4)	22(2)
Cl(7)	4223(6)	9516(2)	6177(4)	18(1)
Cl(8)	1280(7)	11010(2)	6646(4)	18(1)
Cl(9)	-1525(6)	9570(2)	6157(4)	19(2)
O(1)	6060(21)	1856(5)	2343(12)	28(5)
N(1)	-1995(20)	655(7)	-1705(12)	14(3)
N(2)	-5620(19)	1911(6)	-2222(12)	12(3)
N(3)	-4081(21)	963(7)	-3463(13)	18(4)
N(4)	6423(21)	3411(7)	4507(13)	18(3)
N(5)	4440(20)	4326(6)	3469(12)	12(3)
N(6)	-2131(20)	1890(6)	-2483(12)	13(3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 5.3 Bond lengths (Å)

Hg(1)-Cl(3)	2.322 (5)	Hg(1)-Cl(5)	2.316 (5)
Hg(1)-Cl(6)	3.048 (5)	Hg(1)-Cl(1A)	2.952 (4)
Hg(1)-Cl(8A)	3.070 (5)	Hg(2)-Cl(1)	2.601 (4)
Hg(2)-Cl(2)	2.420 (5)	Hg(2)-Cl(4)	2.526 (5)
Hg(2)-Cl(6)	2.414 (4)	Hg(3)-Cl(7)	2.325 (5)
Hg(3)-Cl(8)	2.649 (4)	Hg(3)-Cl(9)	2.352 (5)
Hg(3)-Cl(2A)	3.088 (5)	Co(1)-N(1)	1.992 (15)
Co(1)-N(2)	1.968 (15)	Co(1)-N(3)	1.960 (16)
Co(1)-N(6)	1.961 (15)	Co(1)-N(4A)	1.974 (16)
Co(1)-N(5A)	1.966 (15)	Cl(1)-Hg(1B)	2.952 (4)
Cl(2)-Hg(3A)	3.088 (5)	Cl(8)-Hg(1A)	3.070 (5)
N(4)-Co(1A)	1.974 (16)	N(5)-Co(1A)	1.966 (15)

Table 5.4 Bond angles (°)

Cl(3)-Hg(1)-Cl(5)	176.1(2)	Cl(3)-Hg(1)-Cl(6)	88.6(2)
Cl(5)-Hg(1)-Cl(6)	95.2(2)	Cl(3)-Hg(1)-Cl(1A)	90.4(2)
Cl(5)-Hg(1)-Cl(1A)	91.2(2)	Cl(6)-Hg(1)-Cl(1A)	72.8(1)
Cl(3)-Hg(1)-Cl(8A)	88.0(2)	Cl(5)-Hg(1)-Cl(8A)	88.6(2)
Cl(6)-Hg(1)-Cl(8A)	146.0(1)	Cl(1A)-Hg(1)-Cl(8A)	141.0(1)
Cl(1)-Hg(2)-Cl(2)	102.0(2)	Cl(1)-Hg(2)-Cl(4)	94.5(2)
Cl(2)-Hg(2)-Cl(4)	115.9(2)	Cl(1)-Hg(2)-Cl(6)	100.1(1)
Cl(2)-Hg(2)-Cl(6)	128.7(2)	Cl(4)-Hg(2)-Cl(6)	107.7(2)
Cl(7)-Hg(3)-Cl(8)	105.6(2)	Cl(7)-Hg(3)-Cl(9)	155.1(2)
Cl(8)-Hg(3)-Cl(9)	99.1(2)	Cl(7)-Hg(3)-Cl(2A)	92.9(2)
Cl(8)-Hg(3)-Cl(2A)	87.8(1)	Cl(9)-Hg(3)-Cl(2A)	91.1(2)
N(1)-Co(1)-N(2)	178.2(6)	N(1)-Co(1)-N(3)	90.6(6)
N(2)-Co(1)-N(3)	91.2(6)	N(1)-Co(1)-N(6)	89.2(6)
N(2)-Co(1)-N(6)	90.6(6)	N(3)-Co(1)-N(6)	89.9(7)
N(1)-Co(1)-N(4A)	89.0(6)	N(2)-Co(1)-N(4A)	89.2(6)
N(3)-Co(1)-N(4A)	179.1(7)	N(6)-Co(1)-N(4A)	90.8(6)
N(1)-Co(1)-N(5A)	91.7(6)	N(2)-Co(1)-N(5A)	88.5(6)
N(3)-Co(1)-N(5A)	88.7(6)	N(6)-Co(1)-N(5A)	178.3(7)
N(4A)-Co(1)-N(5A)	90.5(6)		

for *trans*-$[CoCl_2(en)_2]_2[Hg_2Cl_6]$

Table 5.5 Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2 x10^3$)

	x	y	z	U(eq)
Hg(1)	3127(1)	811(1)	339(1)	19(1)
Co(1)	5044(1)	-2821(1)	2631(1)	9(1)
Cl(1)	5743(2)	680(3)	913(1)	15(1)
Cl(2)	7435(2)	-2724(3)	2348(1)	14(1)
Cl(3)	2627(2)	-2914(2)	2893(1)	13(1)
Cl(4)	1477(2)	-1128(2)	772(1)	16(1)
Cl(5)	2667(3)	3288(3)	-138(1)	21(1)
N(1)	4548(8)	-2604(8)	1532(4)	12(2)
N(2)	5060(8)	-5014(9)	2439(5)	17(2)
C(1)	5094(11)	-5291(11)	1595(6)	18(3)
C(2)	4097(10)	-4101(10)	1218(5)	16(3)
N(3)	5023(8)	-642(8)	2817(4)	11(2)
N(4)	5589(9)	-3035(8)	3723(4)	15(2)
C(3)	4988(10)	-343(10)	3677(5)	15(3)
C(4)	5950(10)	-1498(12)	4038(6)	20(3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 5.6 Bond lengths (Å)

Hg(1)-Cl(1)	2.571 (2)	Hg(1)-Cl(4)	2.402 (2)
Hg(1)-Cl(5)	2.369 (3)	Hg(1)-Cl(1A)	2.747 (2)
Co(1)-Cl(2)	2.242 (2)	Co(1)-Cl(3)	2.256 (2)
Co(1)-N(1)	1.957 (7)	Co(1)-N(2)	1.961 (8)
Co(1)-N(3)	1.947 (7)	Co(1)-N(4)	1.955 (8)
Cl(1)-Hg(1A)	2.747 (2)	N(1)-C(2)	1.483 (12)
N(2)-C(1)	1.481 (13)	C(1)-C(2)	1.527 (13)
N(3)-C(3)	1.512 (12)	N(4)-C(4)	1.494 (13)
C(3)-C(4)	1.476 (14)		

Table 5.7 Bond angles (°)

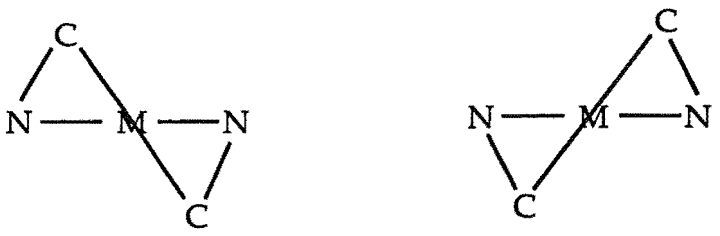
Cl(1)-Hg(1)-Cl(4)	115.4(1)	Cl(1)-Hg(1)-Cl(5)	109.5(1)
Cl(4)-Hg(1)-Cl(5)	131.0(1)	Cl(1)-Hg(1)-Cl(1A)	85.8(1)
Cl(4)-Hg(1)-Cl(1A)	98.6(1)	Cl(5)-Hg(1)-Cl(1A)	103.4(1)
Cl(2)-Co(1)-Cl(3)	178.9(1)	Cl(2)-Co(1)-N(1)	89.7(2)
Cl(3)-Co(1)-N(1)	89.3(2)	Cl(2)-Co(1)-N(2)	89.5(2)
Cl(3)-Co(1)-N(2)	90.5(2)	N(1)-Co(1)-N(2)	86.2(3)
Cl(2)-Co(1)-N(3)	90.6(2)	Cl(3)-Co(1)-N(3)	89.5(2)
N(1)-Co(1)-N(3)	93.5(3)	N(2)-Co(1)-N(3)	179.7(4)
Cl(2)-Co(1)-N(4)	88.9(2)	Cl(3)-Co(1)-N(4)	92.1(2)
N(1)-Co(1)-N(4)	178.6(3)	N(2)-Co(1)-N(4)	93.8(3)
N(3)-Co(1)-N(4)	86.5(3)	Hg(1)-Cl(1)-Hg(1A)	94.2(1)
Co(1)-N(1)-C(2)	109.2(5)	Co(1)-N(2)-C(1)	109.3(6)
N(2)-C(1)-C(2)	106.7(7)	N(1)-C(2)-C(1)	107.1(7)
Co(1)-N(3)-C(3)	109.5(5)	Co(1)-N(4)-C(4)	108.4(6)
N(3)-C(3)-C(4)	106.0(7)	N(4)-C(4)-C(3)	110.2(8)

5.3 Results and Structure Descriptions

X-ray single crystal structure analyses reveal that $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$ consists of a $[Co(NH_3)_6]^{3+}$ cation , a $[Hg_3Cl_9^{3-}]$ anion and a water of crystallization molecule (Figure 5.1) and that *trans*-$[CoCl_2(en)_2]_2[Hg_2Cl_6]$ consists of two *trans*-$[CoCl_2(en)_2]^+$ cations and a dimeric $Hg_2Cl_6^{2-}$ anion (Figure 5.2).

5.3.1 The *trans*-$CoCl_2(en)_2^+$ cation

Ethylenediamine can complex with transition metal ions to form a five-membered chelate ring compound. The ring has a two-fold axis of symmetry and can adopt either δ or λ enantiomeric conformation (Scheme 5.1). Chelate complexes were first investigated at the begining of this century and they have played a very important role in the foundation of coordination chemistry and stereochemistry [59].



δ λ

Scheme 5.1 The δ- and λ- conformations of five-membered chelate ring

trans-bis(ethylenediamine) cation can adopt one of the three stereochemical possibilities: δδ, λλ and δλ. The first two δδ and λλ are enantiomeric and energetically equivalent and are estimated to be 4KJmol^{-1} more stable than the diastereoisomeric δλ form [60]. However in solid state most of the *trans*-bis(ethylenediamine) complexes adopt the slightly less stable δλ form and the ring conformation adopted in all the salts of the *trans*-$CoCl_2(en)_2^+$ cation, so far examined by crystal structure analysis, have the δλ arrangement (Table 5.8) [61-67].

Table 5.8 Ring Conformation in Some *trans*-$[CoCl_2(en)_2]^+$ complexes

Complex	Configuration	Reference
$[CoCl_2(en)_2]Cl{\cdot}HCl{\cdot}2H_2O$	δλ	61
$[CoCl_2(en)_2]NO_3$	δλ	62
$[CoCl_2(en)_2]TlCl_4$	δλ	63
$[CoCl2(en)_2]_2[Hg_2Cl_6]$	δλ	This work
$[CoCl_2(en)_2]ClO_4$	δλ	64
$[CoCl_2(en)_2]_2[CoCl_4]$	δλ	65
$[CoCl_2(en)_2]_2[Se_2S_2O_6]$	δλ	66
$[ClCl_2(en)_2]_2[S_6O_6]$	δλ	67

One of the possibilities could be the reasonably strong influence of crystal packing forces. In an undistorted five-membered chelate ring formed by ethylenediamine coordinated to Co(III), the C-C bond should be at an angle of ±48.8° (dihedral angle) with respect to the N-Co-N plane [68].

The observed dihedral angles in this *trans*-$CoCl_2(en)_2^+$ cation are -48.1° and 50.4°and are reasonably close to this number.

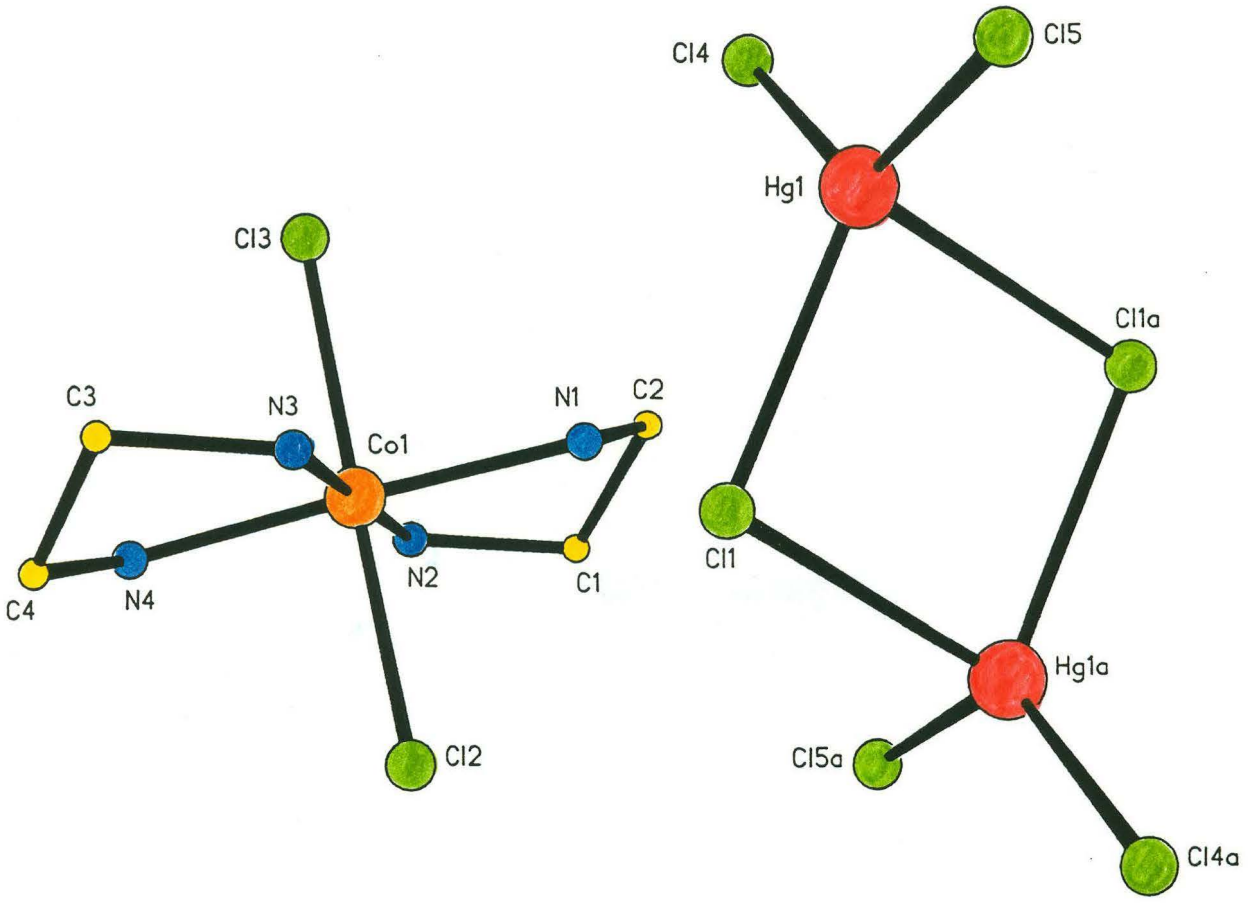


Figure 5.1 The molecular Structure of *trans*-$[CoCl_2(en)_2]_2[Hg_2Cl_6]$

In this cation, there are three types of N-Co-N angles (Figure 5.1). The first group of the three is N-Co-N inside the two five-membered Co(III) ethylenediamine ring at the values of 86.2(3)° and 86.5(3)°. The second and third types of angles are the N-Co-N angle between the two diamine ligands. Mean data for these two sets of angles are 93.6(3)° and 179.1(4)°, respectively. The Cl-Co-Cl angle is 178.9(1)° and is slightly bent away from

180°. The mean Co-Cl bond distance observed in this cation is 2.25(1)Å and is similar to a mean Co-Cl distance of 2.26(1)Å found in monochloro cobalt(III) pentaamine complexes [61-67].

The mean Co-N, N-C and C-C bond lengths in this cation are 1.958(3)Å, 1.49(2)Å and 1.49(4)Å, respectively (Table 5.4).

5.3.2 The $Co(NH_3)_6^{3+}$ cation

The Co-N distances of this cation range 1.964(16)-1.987(15)Å and the N-Co-N bond angles are within 1° of 90° or 2° of 180° (Tables 5.6 and 5.7 and Figure 5.2). Both the bond lengths and bond angles are well consistent with other results for $Co(NH_3)_6^{3+}$ salts (Table 5.9) [69-75].

Table 5.9 Co(III)—NH_3 Bond Distances(Å)

Compound	Co(III)-N(Å)	Reference
$[Co(NH_3)_6][CrO_4]\cdot Cl\cdot 3H_2O$	1.960(4)	69
$[Co(NH_3)_6]CdCl_5$	1.960(6)	70
$[Co(NH_3)_6]I_3$	1.936(15)	71, 72
$[Co(NH_3)_6]Cl_3$	1.963	73
$[Co(NH_3)_6]TlCl_6$	2.07	74
$[Co(NH_3)_6]TlBr_6$	2.02	74
$[Co(NH_3)_6][HgCl_5]$	1.960(6)	39
$[Co(NH_3)_6][ZnCl_4]\cdot Cl$	1.968(11)	75

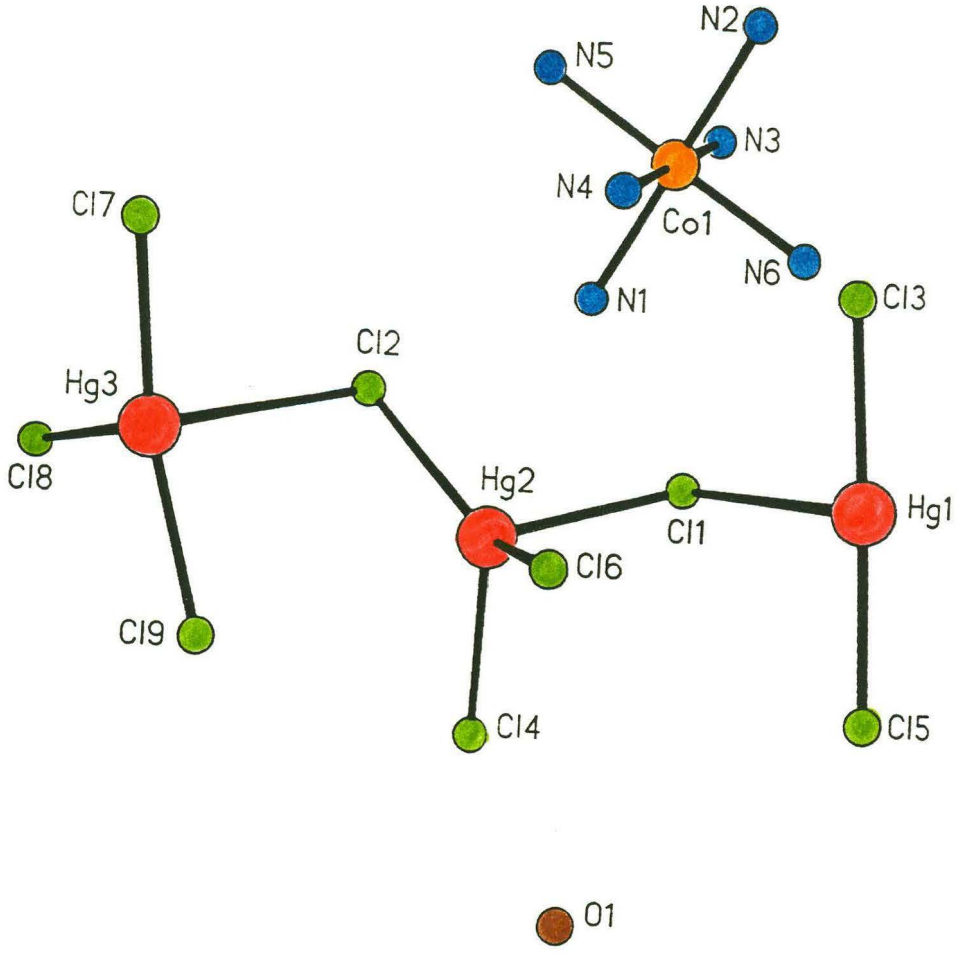
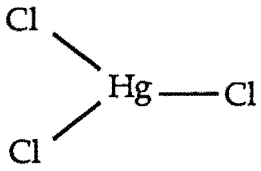


Figure 5.2 The molecular structure of $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$

5.3.3 The $HgCl_3^-$ Anions

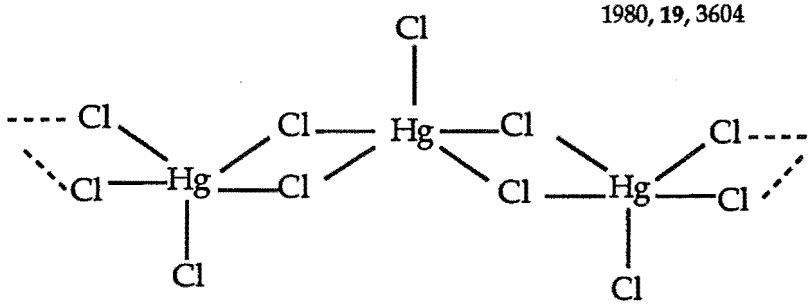
The $HgCl_3^-$ anions can exist as discrete trigonal planar $HgCl_3^-$ units, $(HgCl_3^-)_n$ chain structures or dimeric edge-shared bitetrahedra $Hg_2Cl_6^{2-}$ and now $(Hg_3Cl_9^{3-})_n$ chain structures. Scheme 5.2 shows the relationship between these structural units. However, the factors which cause the anion arrangements from monomer to dimer to polymer are as yet unknown. As the configuration of chloro-mercury(II) anions does not

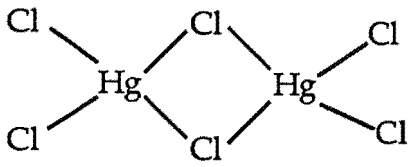
follow from the stoichiometry, X-ray single crystal structure analysis is still the only technique available to make the distinction [40].



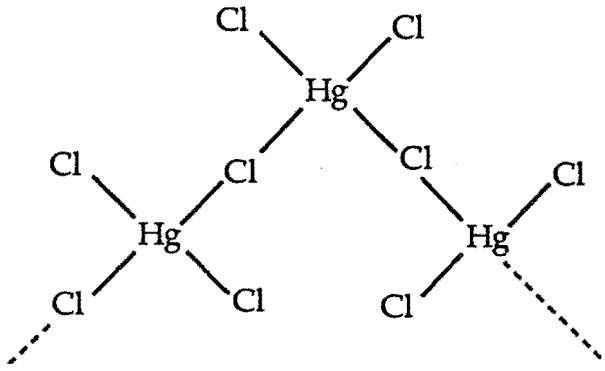
Discrete $HgCl_3^-$ anion
Larock, et al, Organometallics, 1987, **6**, 1780

$(HgCl_3^-)_n$ chain structure
Kistenmacher, et al, Inorg. Chem., 1980, **19**, 3604





$[Hg_2Cl_6]^{2-}$



$\{[Hg_3Cl_9]^{3-}\}_n$

Scheme 5.2 The relationship between $HgCl_3^-$ unit, $(HgCl_3^-)_n$ chain structure, $Hg_2Cl_6^{2-}$ and $(Hg_3Cl_9^{3-})_n$ chain structure

The $Hg_2Cl_6^{2-}$ Anion

The anion found in *trans*-$[CoCl_2(en)_2][HgCl_3]$ is a dimeric $Hg_2Cl_6^{2-}$ unit (Figure 5.1). This $Hg_2Cl_6^{2-}$ anion is found to adopt the centrosymmetric arrangement with a terminal Cl(4)-Hg(1)-Cl(5) bond angle of 131.0(1)°. This anion consists of two symmetry related Hg(II) atoms each with two terminal chloride ions and two bridged chloride ions. Thus each of the Hg(II) atoms has a distorted tetrahedral coordination environment with two short, strong Hg-Cl bonds at the distances of 2.369(2)Å and 2.402(2)Å and two asymmetrically, intermediately strong bridging Hg-Cl bonds at the distances of 2.571(2)Å and 2.747(2)Å with the Cl-Hg-Cl bond angles ranging from 85-131°. It is similar to the anion of $[H_2en][Hg_2Cl_6]$ reported in chapter 4 however it adopts a more asymmetric bridging system compared with the previously reported one. For the previously reported $Hg_2Cl_6^{2-}$ anion, the independent Hg-Cl bridging distances are at 2.751(3)Å and 2.811(5)Å but for this $Hg_2Cl_6^{2-}$ anion the bridging Hg-Cl distances are at 2.571(2)Å and 2.747(2)Å, respectively. The relatively short and strong bridging Hg-Cl bonds also lead the terminal Cl-Hg-Cl bond angle in this structure towards more "close" (further away from 180°) structural arrangement compared with the previous structure (Table 4.8). The Hg-Cl bond lengths and Cl-Hg-Cl bond angles in this compound are quite comparable to those obtained previously for $Hg_2Cl_6^{2-}$ units (Tables 4.3 & 4.4 and Tables 5.3 & 5.4). The closer Cl-Hg-Cl terminal angles with shorter Hg-Cl terminal bonds give more distortion from linearity for the $HgCl_2$ subunits and closer arrangement towards tetrahedral coordination environment for the $HgCl_4$ subunits. The structure packing network (Figure 5.3) of this compound shows that there is a very long Hg···Cl interaction between the Hg(1) and Cl(3) from the cations *trans*-$[CoCl_2(en)_2]^+$ at the distance of ~3.34Å. Thus we may consider that Hg(II) atom in this structure is five coordinate with a fifth very long, weak Hg···Cl interaction of 3.34Å, but this weak interaction hardly distorts the $Hg_2Cl_6^{2-}$ anion.

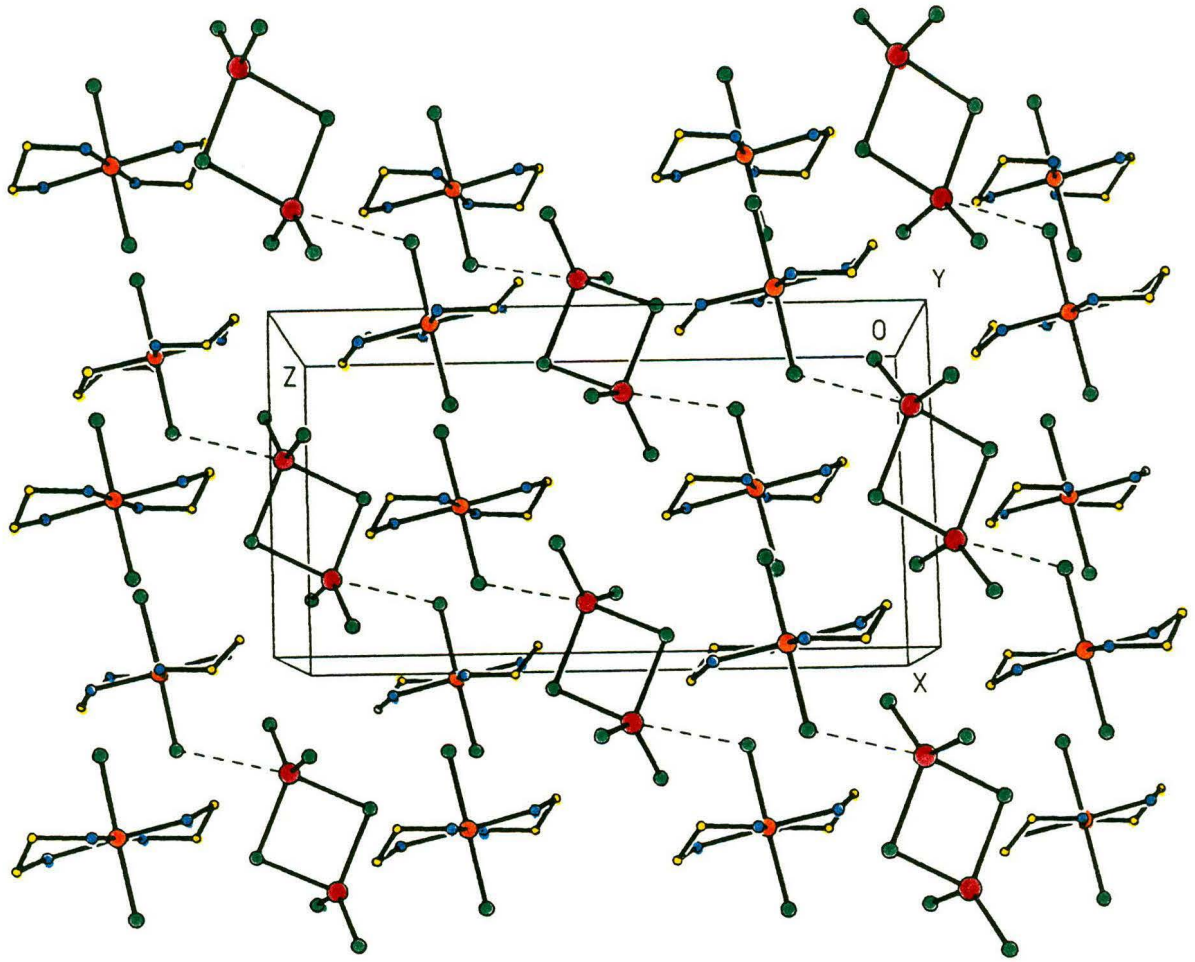


Figure 5.3 The packing diagram of *trans*-$[CoCl_2(en)_2]_2[Hg_2Cl_6]$

The $\{Hg_3Cl_9^{3-}\}_n$ Anion

The $Hg_3Cl_9^{3-}$ anion found in $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$ has a chain structure (Figure 5.2). It can be regarded as made from single chloro-bridged $\{HgCl_3^{-}\cdots HgCl_4^{2-}\cdots HgCl_2\}$ sub-units. The packing diagram of this compound is shown in Figure 5.4.

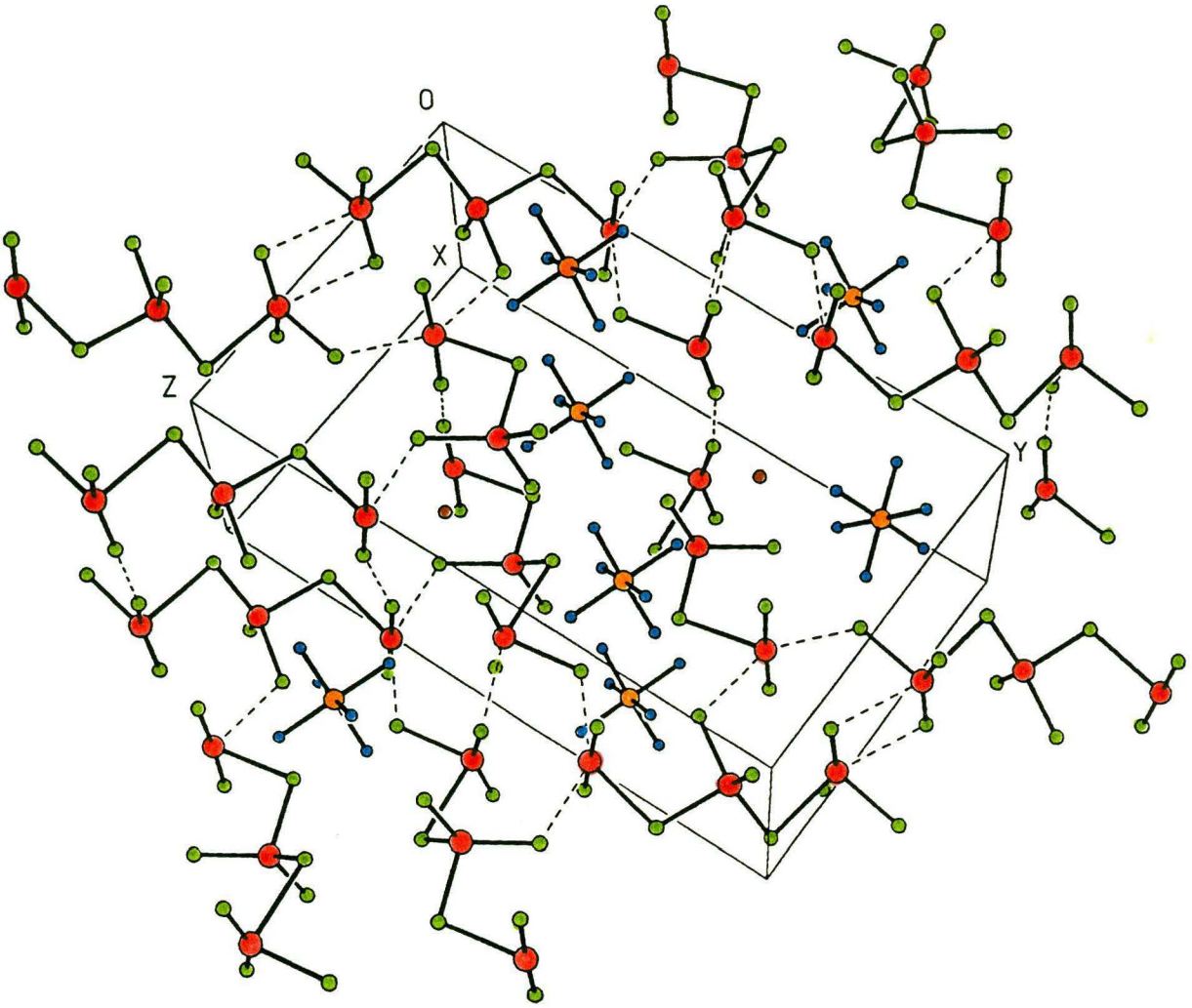


Figure 5.4 The packing diagram of $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$

The central $HgCl_4^{2-}$ sub-unit [Hg(2)], has an approximately tetrahedral coordination environment with bond lengths ranging from 2.41-2.60Å and bond angles ranging from 94-128°, very similar to those found in the isolated $HgCl_4^{2-}$ unit [40, 48]. This central $HgCl_4^{2-}$ sub-unit also links, on either side, to the two bridging chloride ions Cl(1) and Cl(2) to $HgCl_2$ and

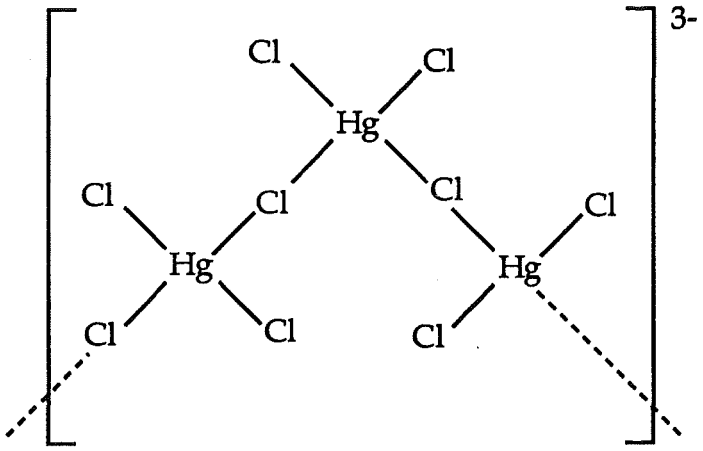
$HgCl_3^-$ sub-units with Hg-Cl distances of Cl(1)-Hg(1) 2.952(4) and Cl(2)-Hg(3) 3.088(5)Å, respectively.

Hg(3) atom is also a four coordinate sub-unit with two short Hg-Cl bonds [Hg(3)-Cl(7) 2.325(5)Å and Hg(3)-Cl(9) 2.352(5)Å], one moderate Hg-Cl bond [Hg(3)-Cl(8) 2.649(4)Å] and one long Hg-Cl bond [Hg(3)-Cl(2) 3.088(5)Å]. It also can be regarded as a very distorted tetrahedron.

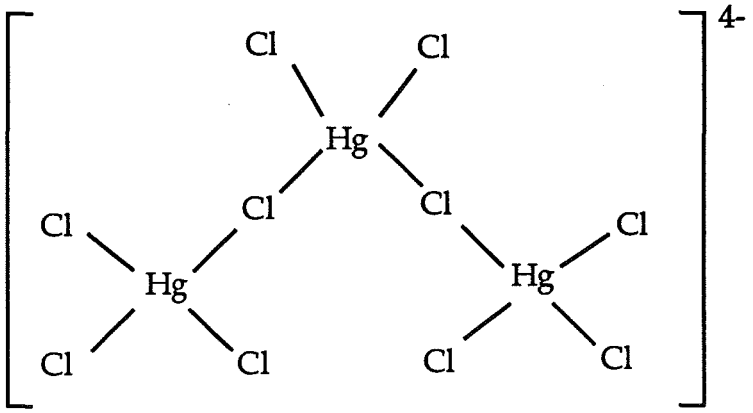
Hg(1), at the other end of the $Hg_3Cl_9^{3-}$ unit, is three coordinate with two short Hg-Cl bonds [Hg(1)-Cl(3) 2.322(5)Å and Hg(1)-Cl(5) 2.316(5)Å] and one long Hg-Cl bond [Hg(1)-Cl(1) 2.952(4)Å]. The Cl(3)-Hg(1)-Cl(5) bond angle of 176.1(2)° indicates that the linearity of $HgCl_2$ is well retained in this sub-unit.

From the packing diagram of $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$ (Figure 5.4), we can see that Hg(1) atom also links to Cl(6) and Cl(8) atoms in the adjacent $Hg_3Cl_9^{3-}$ units at distances of 3.048(5)Å and 3.070(5)Å, respectively, to form a three dimensional packing network in this crystal structure. The Cl(6) and Cl(8) atoms act as the connectors joining the $Hg_3Cl_9^{3-}$ units into an infinite structure. It is also shown in this packing diagram that Cl(9) bridges to Hg(3) through a very long , weak non-bonding interaction at a distance 3.34Å to complete this packing network. Thus we conclude that the Hg(1) is formally five-coordinate with three moderate-long Hg-Cl bonds and two short Hg-Cl bonds in this structure but the Hg(3) achieves five-coordinate with one very long Hg···Cl interaction, one moderate-long Hg-Cl bond, one moderate Hg-Cl bond and two short Hg-Cl bonds.

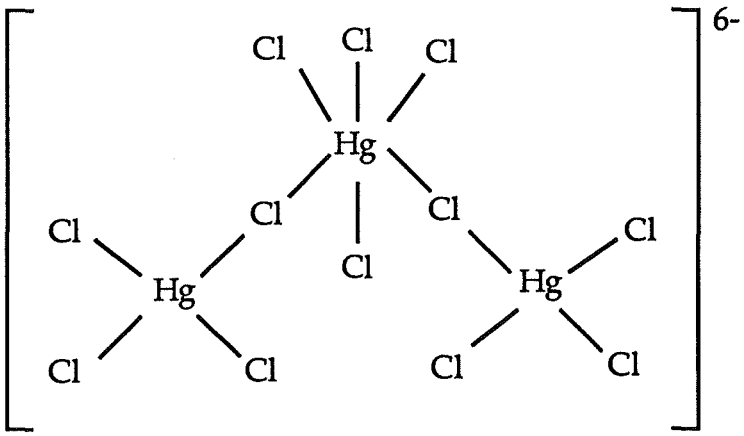
Also we can compare the $\{Hg_3Cl_9^{3-}\}_n$ units with two previously characterized $Hg_3Cl_x^{n-}$ anions, viz. discrete $Hg_3Cl_{10}^{4-}$ and $Hg_3Cl_{12}^{6-}$ anions [76]. The relationship between these chloro-mercury(II) anion systems is shown in Scheme 5.3.



$\{[Hg_3Cl_9]^{3-}\}_n$



$[Hg_3Cl_{10}]^{4-}$



$[Hg_3Cl_{12}]^{6-}$

Scheme 5.3 The relationship between $(Hg_3Cl_9^{3-})_n$, $Hg_3Cl_{10}^{4-}$ and $Hg_3Cl_{12}^{6-}$

In comparison, it can be clearly seen, that by removing two chlorides from the central Hg atom in the $Hg_3Cl_{12}^{6-}$ anion, we get the $Hg_3Cl_{10}^{4-}$ anion, and by removing one of the terminal chloride ions from the $Hg_3Cl_{10}^{4-}$ discrete anion, we get the $Hg_3Cl_9^{3-}$ unit. This diagram also shows that because of removing of one of the terminal chloride ions in $Hg_3Cl_{10}^{4-}$ anion, the terminal Hg(II) atom in $Hg_3Cl_9^{3-}$ unit links to other chlorides in adjacent $Hg_3Cl_9^{3-}$ units to form the infinite $Hg_3Cl_9^{3-}$ structure. This is well illustrated in the packing diagram of $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$ (Figure 5.4).

Chapter 6

Preparation and X-ray Crystal Structure Determination of $[H_4trien][Hg_2Cl_8]$ Complex

6.1 Introduction

In chapter 4 we discussed the crystal structures of $[H_2en]_2{\cdot}[HgCl_4]{\cdot}[Cl]_2$ and $[H_2en]{\cdot}[Hg_2Cl_6]$ complexes and in chapter 5, we dealt with $[Co(NH_3)_6]{\cdot}[Hg_3Cl_9]{\cdot}H_2O$. In both $[H_2en]{\cdot}[Hg_2Cl_6]$ and $[Co(NH_3)_6]{\cdot}[Hg_3Cl_9]{\cdot}H_2O$, the anion structures follow from the charges of counter cations. We have also considered other existing chloro-mercury(II) anions and found that sometimes the configuration of the anions is structurally related to their counter cation charges. For example, in $[Co(NH_3)_6^{3+}][HgCl_5^{3-}]$, the integrity of the anion is maintained in the structure rather than the possible $[HgCl_4^{2-}][Cl^-]$ combination. Although we had found that there had been many $HgCl_4^{2-}$ and $Hg_2Cl_6^{2-}$ anions reported we were not aware of any report of the existence of the $Hg_2Cl_8^{4-}$ anion. Accordingly , we concluded that if we used the 4+ counter cation, we may be able to get either $HgCl_6^{4-}$ or $Hg_2Cl_8^{4-}$ as chloro-mercury(II) anions. We chose triethylenetetramine (trien) as the cation, calculated the proper amounts of reactants trien and $HgCl_2$ for the postulated compounds $[H_4trien][HgCl_6]$ and $[H_4trien][Hg_2Cl_8]$ and attempted to synthesize them. We obtained only one kind of compound: $[H_4trien][Hg_2Cl_8]$.

6.2 Experimental

6.2.1 Preparation of $[H_4trien]{\cdot}[Hg_2Cl_8]$ single crystals

We postulated, at the beginning, that there could be two different complexes $[H_4trien][HgCl_6]$ (1) and $[H_4trien][Hg_2Cl_8]$ (2) which could be synthesized from the equations:

$$\mathbf{trien + HgCl_2 + 4HCl \rightarrow [H_4trien][HgCl_6]}$$
$$\mathbf{trien + 2HgCl_2 + 4HCl \rightarrow [H_4trien][Hg_2Cl_8].}$$

We prepared both of the postulated complexes by dissolving 2.6ml (1) [1.3ml (2)] trien and 4.7g (1) [4.7g (2)] $HgCl_2$ in ~100ml water and ~50ml 3M HCl separately and mixed the solutions. On cooling and leaving the beakers open at room temperature for a few days, colourless crystals deposited. We checked both of the crystals using X-ray single crystal diffractometer and found that there were the same: $[H_4trien][Hg_2Cl_8]$.

Table 6.1 Crystal Data for $[H_4trien][Hg_2Cl_8]$

Complex	$[H_4trien][Hg_2Cl_8]$
Molecular formule	$C_6H_{22}N_4Cl_8Hg_2$
Formular weight	835.2
Crystal size (mm)	0.80x0.20x0.08
Space group	Monoclinic, $P2_1/c$
a(Å)	11.892(3)
b(Å)	11.872(4)
c(Å)	14.350(4)
β(°)	98.25(2)
V(Å^3)	2005.2
D_{calc}(g/cc)	2.77
Temperature (K)	153
F(000)	1544
Linear absorption coefficient (cm^{-1})	164.70
Transmission factors	0.581, 0.295
Merge	0.020
Scan mode	ω
Octants	h, k, ±l
$2\theta_{max}$(°)	52
Reflections measured	3890
Reflections used	2213
Parameters refined	171
Weighting (gx10^3)	6.00
GOOF	1.16
R	4.61
Rw	4.18

6.2.2 X-ray Crystal Structure Determination

Crystal data for this compound are listed in Table 6.1. Atomic coordinates for the non-hydrogen atoms are listed in Table 6.2 and bond lengths and bond angles are listed in Tables 6.3 and 6.4.

for $[H_4trien][Hg_2Cl_8]$

Table 6.2 Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2 x10^3$)

	x	y	z	U(eq)
Hg(1)	2669(1)	1971(1)	1079(1)	19(1)
Hg(2)	7596(1)	1760(1)	1327(1)	22(1)
Cl(1)	5222(3)	1676(4)	1102(3)	19(1)
Cl(2)	8117(4)	2007(4)	2995(3)	24(1)
Cl(3)	7639(4)	3638(4)	527(3)	23(1)
Cl(4)	2869(4)	464(4)	2194(3)	22(1)
Cl(5)	2907(4)	3912(4)	1998(3)	24(1)
Cl(6)	2623(4)	2821(4)	-457(3)	26(1)
Cl(7)	7641(4)	211(4)	256(3)	27(2)
Cl(8)	253(3)	1887(4)	855(3)	20(1)
N(2)	282(14)	4520(12)	1272(9)	22(5)
C(4)	4976(17)	4803(15)	9455(11)	24(6)
C(1)	289(14)	4021(15)	2926(11)	19(6)
C(3)	-89(14)	5301(14)	475(10)	18(4)
N(4)	4742(13)	1074(12)	8832(10)	25(5)
N(1)	-356(12)	4239(14)	3745(9)	23(5)
C(2)	-157(14)	4802(14)	2132(11)	14(4)
N(3)	5182(12)	3575(12)	9480(9)	20(5)
C(5)	5226(14)	3111(16)	8519(10)	20(5)
C(6)	5582(15)	1872(16)	8523(12)	27(4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 6.3 Bond lengths (Å)

Hg(1)-Cl(1)	3.046 (4)	Hg(1)-Cl(4)	2.385 (4)
Hg(1)-Cl(5)	2.644 (4)	Hg(1)-Cl(6)	2.412 (4)
Hg(1)-Cl(8)	2.841 (4)	Hg(2)-Cl(1)	2.791 (4)
Hg(2)-Cl(2)	2.398 (4)	Hg(2)-Cl(3)	2.507 (5)
Hg(2)-Cl(7)	2.398 (5)	N(2)-C(3)	1.486 (20)
N(2)-C(2)	1.444 (22)	C(4)-N(3)	1.476 (23)
C(4)-C(4A)	1.623 (32)	C(1)-N(1)	1.511 (23)
C(1)-C(2)	1.503 (23)	C(3)-C(3A)	1.577 (31)
N(4)-C(6)	1.487 (24)	N(3)-C(5)	1.489 (20)
C(5)-C(6)	1.527 (27)		

Table 6.4 Bond angles (°)

Cl(1)-Hg(1)-Cl(4)	84.5(1)	Cl(1)-Hg(1)-Cl(5)	93.4(1)
Cl(4)-Hg(1)-Cl(5)	108.9(1)	Cl(1)-Hg(1)-Cl(6)	87.1(1)
Cl(4)-Hg(1)-Cl(6)	155.5(2)	Cl(5)-Hg(1)-Cl(6)	94.4(1)
Cl(1)-Hg(1)-Cl(8)	169.6(1)	Cl(4)-Hg(1)-Cl(8)	92.9(1)
Cl(5)-Hg(1)-Cl(8)	96.9(1)	Cl(6)-Hg(1)-Cl(8)	91.2(1)
Cl(1)-Hg(2)-Cl(2)	103.4(1)	Cl(1)-Hg(2)-Cl(3)	93.7(1)
Cl(2)-Hg(2)-Cl(3)	109.1(2)	Cl(1)-Hg(2)-Cl(7)	90.8(1)
Cl(2)-Hg(2)-Cl(7)	134.8(2)	Cl(3)-Hg(2)-Cl(7)	112.5(2)
C(3)-N(2)-C(2)	114.0(14)	N(3)-C(4)-C(4A)	106.1(15)
N(1)-C(1)-C(2)	108.6(14)	N(2)-C(3)-C(3A)	108.6(17)
N(2)-C(2)-C(1)	111.8(14)	C(4)-N(3)-C(5)	111.7(13)
N(3)-C(5)-C(6)	113.4(13)	N(4)-C(6)-C(5)	114.5(15)

The structure was solved by conventional Patterson and Fourier methods and refined by blocked-cascade least-squares procedures. Mercury and chlorine atoms were located from the Patterson map. The lighter atoms, carbon and nitrogen were found from the difference Fourier map and were refined well. Both mercury and chlorine atoms were refined with anisotropic thermal parameters and the hydrogen atoms were inserted at calculated positions using a riding model with the thermal parameters fixed at 0.05. The largest difference peak is 3.19eÅ^{-3} and the largest difference hole is -1.43eÅ^{-3} and they lie close to the mercury(II) position.

6.3 Results and Structure Description

The triethylentetramine chloromercurate(II) salt has proved to be [H_4trien][Hg_2Cl_8] (monoclinic) by the X-ray crystal structure analysis. It consists of an $Hg_2Cl_8^{4-}$ anion and two halves of the two crystallographically independent, discrete, counter cations $[H_4trien]^{4+}$ (Figure 6.1).

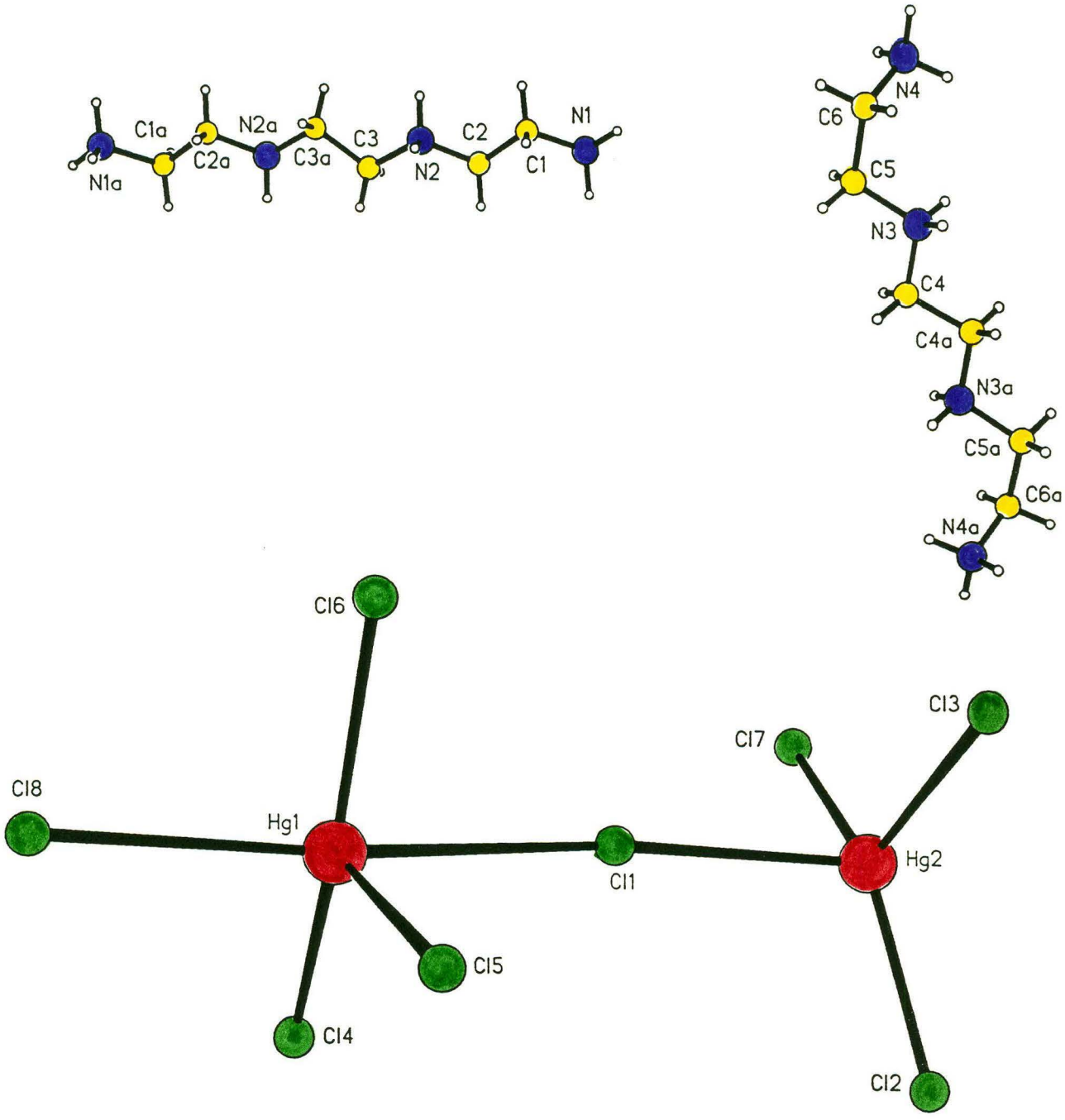


Figure 6.1 The molecular structure of $[H_4trien]^{4+}$ and $[Hg_2Cl_8]^{4-}$

6.3.1 The (H_4trien^{4+}) counter cations

X-ray crystal structure analysis revealed that there are two crystallographically independent $[H_4trien]^{4+}$ cations (I) and (II) in the crystal (Figure 6.1). Each of them has a crystallographic centre of symmetry. In triethylentetramine molecule, the N-C-C-N fragments can adopt either *gauche* or *trans* configurations. In these two triethylentetramine cations of

$[H_4trien]^{4+}$, (I) have the *trans, trans, trans* configuration with N-C-C-N dihedral angles -172.3°, 180.0° and 172.3°, respectively but (II) adopts the *gauche, trans, gauche* configuration with N-C-C-N dihedral angles 68.1°, 180.0° and -68.1°, respectively. The dihedral angle 68.1° found in cation (II) is similar to that of 69.2° in $[H_2en]_2[HgCl_4][Cl]_2$ discussed in Chapter 4 and is well within the range of 63-70° [68] for *gauche* configuration. Because these two cations have intra-crystallographic centres of symmetry both of them have centro-*trans*-N-C-C-N with the dihedral angle of 180.0°. This cation has been described previously in the structure of $[H_4trien][CuCl_4][Cl]_2$ but without any crystallographic details [77].

6.3.2 The $Hg_2Cl_8^{4-}$ anion

Figure 6.1 also shows the arrangement of the $Hg_2Cl_8^{4-}$ anion itself. It can be regarded as two $HgCl_4^{2-}$ units linked together through a Hg···Cl interaction at the distance of 3.046(4)Å. It is similar to that of the anionic structure found in the $[H_2en]\cdot[HgCl_4]\cdot[Cl]_2$ (Chapter 4) compound. In the $[H_2en]\cdot[HgCl_4]\cdot[Cl]_2$ crystal structure these $HgCl_4^{2-}$ units are linked into chains through a long, weak Hg···Cl interaction at 3.28Å. However, in the present structure, the two $HgCl_4^{2-}$ units are linked together through a moderately strong interaction at a distance of 3.046(4)Å. This interaction (3.05Å) is much stronger than that of 3.28Å found in the previous structure thus we consider, here, that in this $[H_4trien][Hg_2Cl_8]$ crystal structure, the $Hg_2Cl_8^{4-}$ exists as an integral unit. The Cl(1) atom bridges to both Hg(1) and Hg(2) atoms at the distances of 3.046(4) and 2.791(4)Å, respectively. Figure 6.2 shows the actual packing structure of this compound in the crystal.

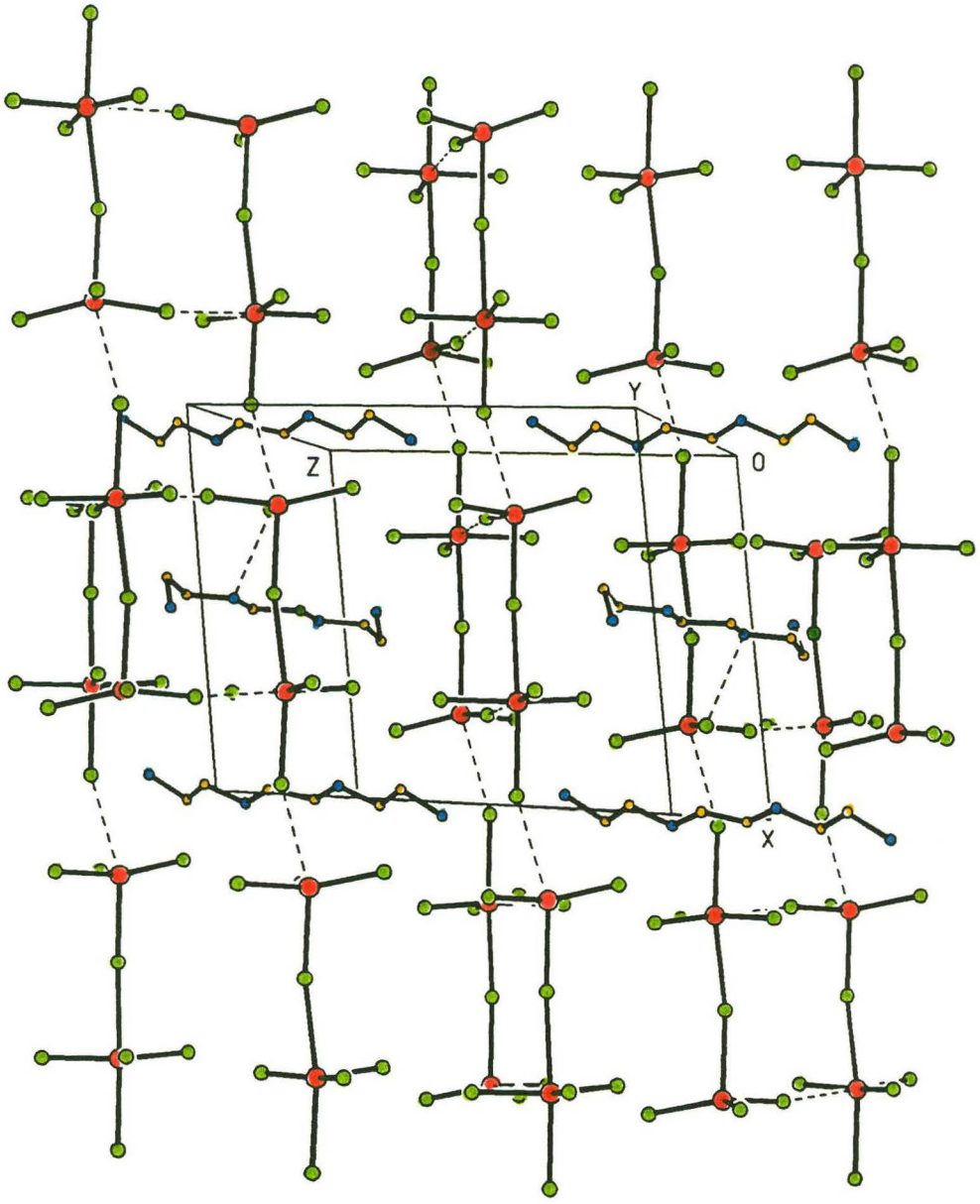


Figure 6.2 The packing diagram of [H_4trien][Hg_2Cl_8]

We can see from the packing network that Hg(1) atoms also cross-link to Cl(7) at the distance of 3.20Å and Hg(2) atoms link to Cl(8) through a very long, weak interaction of 3.32Å, to form a continuous ribbon structure. In the $Hg_2Cl_8^{4-}$ anion, Hg has a heavily distorted bi-pyramidal coordination environment with bond lengths ranging 2.38-3.05Å and bond angles

ranging from 84-156Å (two short Hg-Cl bonds [Hg(1)-Cl(4) 2.385(5)Å and Hg(1)-Cl(6) 2.412(4)Å], two intermediate Hg-Cl bonds [Hg(1)-Cl(5) 2.644(5)Å and Hg(1)-Cl(8) 2.841(4)Å] and a long Hg-Cl bond [Hg(1)-Cl(1) 3.046(4)Å]). However Hg(2) has a distorted tetrahedral coordination sphere with two short, strong Hg-Cl bonds (2.398(4)Å and 2.398(5)Å) and two intermediate Hg-Cl bonds (2.507(5)Å and 2.791(4)Å) with bond angles ranging 90-136°. From our final analysis we conclude that Hg(1) is six coordinate with a sixth of Hg···Cl contact of 3.20Å and Hg(2) has 5 coordinate with a fifth Hg···Cl distance of 3.32Å.

There are some other $HgCl_4^{2-}$ combinations besides those we have discussed above. For example, in $[Cr(en)_3^{3+}]_2[HgCl_4^{2-}]_3$ [44], the crystal structure of which was amongst some of the early work done in this department, it is found that the anion $[HgCl_4^{2-}]_3$ consisted of three $HgCl_4^{2-}$ units. One of them was a completely discrete $HgCl_4^{2-}$ unit and the other two $HgCl_4^{2-}$ units were drawn together with the Hg···Hg distance 3.60Å (Figure 6.3).

For this $HgCl_4^{2-}$···$HgCl_4^{2-}$ fragment, the two $HgCl_4^{2-}$ units are found to have very similar structures with bond lengths ranging from 2.48-2.61Å for both and bond angle ranging from 94.7-136.5° for (1) and 92.8-135.6° for (2) (Figure 6.3). The two $HgCl_4^{2-}$ units staying on the top of each other adopt an eclipsed configuration in this structure rather than a staggered one. If we link Hg(2)···Cl(31), Hg(2)···Cl(32) and Hg(3)···Cl(21), Hg(3)···Cl(23), we find that both Hg(II) ions could achieve octahedral coordination environments even if the distances are very long (3.35-3.73Å) (Figure 6.3).

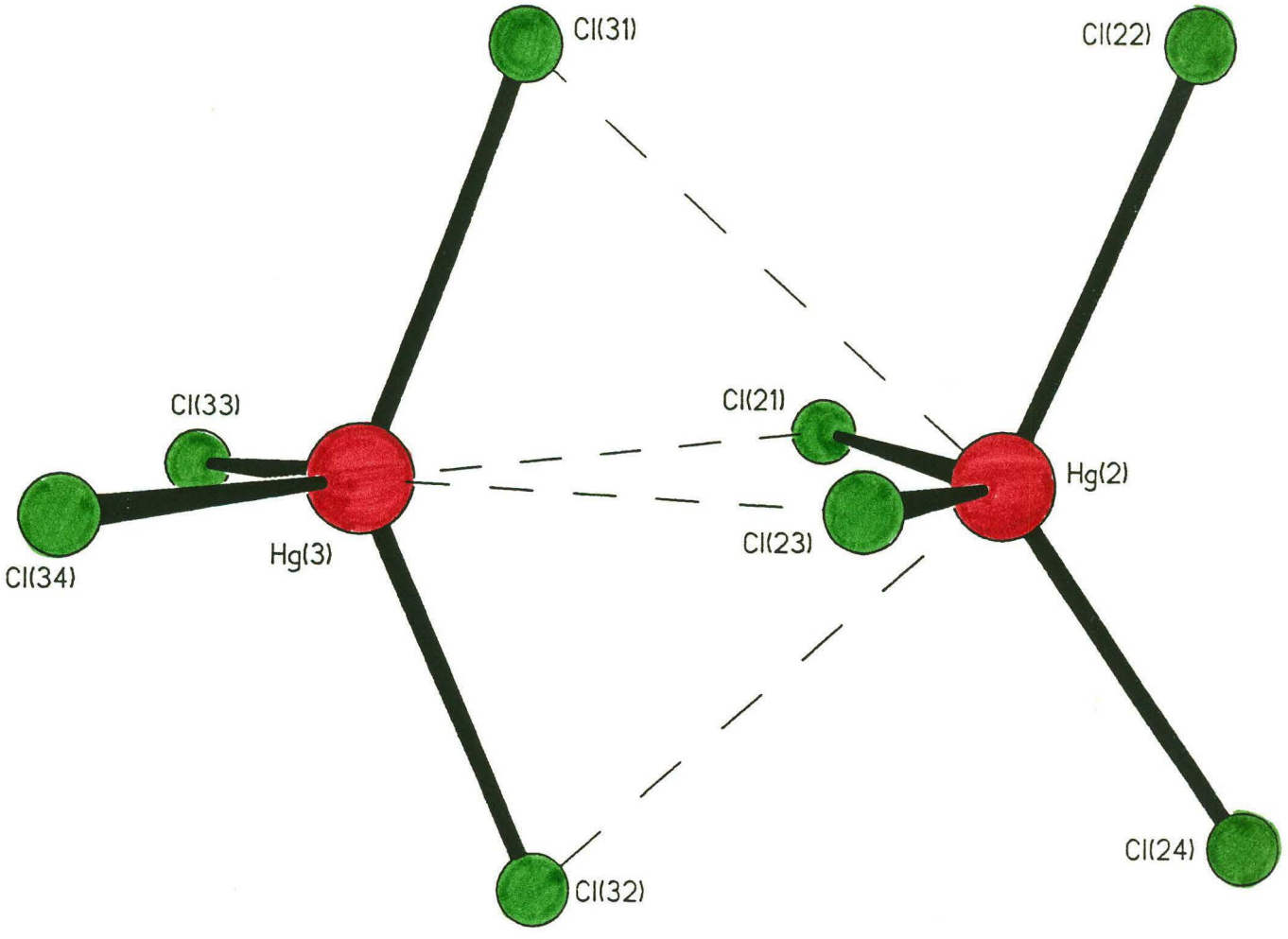


Figure 6.3 The labelling diagram of the two overlapped $[HgCl_4]^{2-}$ anions

Also if we link Cl···Cl atoms together for each equivalent pair in this $[HgCl_4^{2-}]_2$ fragment we get Cl···Cl distances ranging from 3.78-4.03Å. These distances are very long indeed but are still within the range of 3.27-4.10Å for Cl···Cl contacts [20]. So we consider, here, that these two $HgCl_4^{2-}$···$HgCl_4^{2-}$ units are drawn together, with an eclipsed configuration, by both the Hg···Cl long distance attractions and the Cl···Cl long distance attractions. The two

Hg(II) atoms have coordination numbers between four and six and since they can not achieve a regular octahedral environment the two $HgCl_4^{2-}$ units exist in the packing arrangement as a "frozen" state. So far we have discussed at least three different types of $HgCl_4^{2-}$ combinations: (1) $HgCl_4 \cdots ClHgCl_3$ in $[H_2en]_2[HgCl_4][Cl]_2$; (2) $Hg_2Cl_8^{4-}$ in $[H_4trien][Hg_2Cl_8]$ and (3) $HgCl_4^{2-} \cdots HgCl_4^{2-}$ in $[Cr(en)_3^{3+}]_2[HgCl_4^{2-}]_3$. Once again we can see that there is a very rich diversity among chloro-mercury(II) anionic structures and X-ray single crystal structure analysis is the only available technique to make the distinctionbetween them.

As far as we are aware, the existence of the $Hg_2Cl_8^{4-}$ anion has not been reported before.

Chapter 7

The X-ray Crystal Structure Determination of [*cis*-$PtCl_2(NH_3)_2 \cdot (HgCl_2)_3]_n$

7.1 Introduction

cis-Diamminedichloroplatinum(II)(*cis*-DDP or cisplatin) is widely used in antitumor cancer therapy [78] and is one of the most effective anticancer agents available at present [79]. A great amount of evidence indicates that *cis*-DDP has shown its strong biological activity by binding to DNA and inhibiting replication. Furthermore, the characteristic modes by which *cis*-DDP binds to DNA have been defined [80]. However, although discovered over twenty years ago by Barnett Rosenberg and coworkers [81], the mode of action of Cisplatin, as the drug is now generally called, is not completely understood [82]. This is mainly because the interactions of model ions in physiological systems are very complex [83]. Cisplatin has been a clinically important antitumour drag used in hospitals all over the world, in the treatment of advanced metastatic, testicular and ovarian cancers [80]. Currently, the study on the hydrolysis kinetics of this compound and the anation kinetics of the products, under a variety of pH and ionic strength conditions is being carried out in this department [84-86]. Some kinetics studies in this area involve either Hg^{2+} or Pb^{2+}, as the metal ion assisting the halide release [87], because the formation of a precipitate limits the methods available to monitor the reaction and heterogeneous systems are often subject to complicating surface effects.

In order to assist the study of the kinetics, we solved the crystal structure of the adduct of $HgCl_2$ and *cis*-DDP (ie, [*cis*-$PtCl_2(NH_3)_2 \cdot (HgCl_2)_3]_n$) and report the results here.

7.2 Experimental

7.2.1 Preparation of The Crystals

To a solution of 0.03M $HgCl_2$ in 0.1M $HClO_4$ (20ml) was added 20 mg of *cis*-$PtCl_2(NH_3)_2$. This mixture was heated at 60°C for about 2 hrs and then allowed to cool slowly to room temperature in the dark. Pale yellow needle–like crystals, suitable for single crystal X-ray analysis, deposited over the next 48 hours. Crystals were provided by Dr. Sian E. Miller and Dr. Donald House.

7.2.2 X-ray Crystal Structure Determination

Crystal data for this cisplatin are listed in Table 7.1. Intensity data for a small elongated rod-like crystal were collected with a Nicolet R3m four-circle diffractometer at -120°C. Graphite monochromated MoKα radiation (λ=0.71069Å) was used, with fixed omega scans. The collected intensities were corrected for absorption effects.

The structure was solved by conventional Patterson and Fourier methods and refined by blocked-cascade least-squares procedures. The Pt and Hg atoms were distinguished on the basis of chemical reasoning, and all atoms heavier than N were refined with anisotropic thermal parameters. In the last cycles of refinement, the ammonia hydrogen atoms were included in their calculated positions. The non-hydrogen atom coordinates are listed in Table 7.2. Bond lengths and bond angles are listed in Tables 7.3 and 7.4. The final difference Fourier map shows that the largest difference peak is 4.42eÅ^{-3} and the largest difference hole is -9.24eÅ^{-3}. They lie close to the mercury and platinum atoms.

Table 7.1 Crystal data

Complex	$Pt(NH_3)_2Cl_2 \cdot (HgCl_2)_3$
Molecular formule	$H_6N_2Cl_8PtHg_3$
Formula weight	1114.5
Crystal size (mm)	0.10x0.12x0.48
Space group	monoclinic
	C2/c
a(Å)	18.532(5)
b(Å)	6.506(2)
c(Å)	12.492(4)
β(°)	98.76(3)
V(Å^3)	1485.5(8)
Z	4
$D_{calc(g/cc)}$	4.98
Temperature (K)	153
F(000)	1859
Linear absorption coefficient (cm^{-1})	418.21
Transmission factors	0.192, 0.331
Merge	0.026
Scan mode	ω
Octants	h, k, ±l
$2\theta_{max}$(°)	60
Reflections measured	2179
Reflections used	1653
Parameters refined	61
Weighting (gx10^3)	5.55
GOOF	0.84
R	5.91
R_w	6.30

for *cis*-$[PtCl_2(NH_3)_2]\cdot[HgCl_2]_3$

Table 7.2 Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2 x10^3$)

	x	y	z	U(eq)
Hg(1)	0	0	0	10(1)
Pt(1)	0	2399(1)	2500	5(1)
Hg(2)	1996(1)	148(1)	-792(1)	11(1)
Cl(1)	-637(2)	-2911(7)	342(3)	11(1)
Cl(2)	1504(2)	-2669(7)	-60(4)	14(1)
Cl(3)	2550(2)	2841(8)	-1540(4)	16(1)
N(1)	788(9)	4608(25)	2312(13)	12(3)
Cl(4)	853(2)	-83(7)	2250(3)	10(1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 7.3 Bond lengths (Å)

Hg(1)-Cl(1)	2.305 (5)	Hg(1)-Cl(4)	3.003 (4)
Hg(1)-Cl(1A)	2.305 (5)	Hg(1)-Cl(4A)	3.003 (4)
Pt(1)-N(1)	2.087 (17)	Pt(1)-Cl(4)	2.313 (5)
Pt(1)-N(1A)	2.087 (17)	Pt(1)-Cl(4C)	2.313 (5)
Hg(2)-Cl(2)	2.297 (5)	Hg(2)-Cl(3)	2.299 (5)
Hg(2)-Cl(4B)	2.979 (4)	Cl(4)-Hg(2A)	2.979 (4)

Table 7.4 Bond angles (°)

Cl(1)-Hg(1)-Cl(4)	91.4(1)	Cl(1)-Hg(1)-Cl(1A)	180.0(1)
Cl(4)-Hg(1)-Cl(1A)	88.6(1)	Cl(1)-Hg(1)-Cl(4A)	88.6(1)
Cl(4)-Hg(1)-Cl(4A)	180.0(1)	Cl(1A)-Hg(1)-Cl(4A)	91.4(1)
N(1)-Pt(1)-Cl(4)	87.8(5)	N(1)-Pt(1)-N(1A)	93.0(9)
Cl(4)-Pt(1)-N(1A)	178.4(4)	N(1)-Pt(1)-Cl(4C)	178.4(4)
Cl(4)-Pt(1)-Cl(4C)	91.5(2)	N(1A)-Pt(1)-Cl(4C)	87.8(5)
Cl(2)-Hg(2)-Cl(3)	176.4(2)	Cl(2)-Hg(2)-Cl(4B)	92.2(1)
Cl(3)-Hg(2)-Cl(4B)	89.1(1)	Hg(1)-Cl(4)-Pt(1)	80.8(1)
Hg(1)-Cl(4)-Hg(2A)	166.7(2)	Pt(1)-Cl(4)-Hg(2A)	108.4(2)

7.3 Results and Structure Description

The crystal structure of *cis*-$Pt(NH_3)_2Cl_2$ itself, was determinated in the 1960s [88]. It revealed a square planar stereochemistry in which the intramolecular bond lengths were Pt-Cl=2.33(1)Å and Pt-N=2.01(4)Å and the only bond angle which significantly differed from 90° was Cl-Pt-Cl=91.4°. In 1984, the X-ray single crystal structure of its DMF adduct $PtCl_2(NH_3)_2$·DMF was determined by Raudaschl, et al [89]. In this structure, the geometry around the platinum(II) has square planar coordination with the platinum atom sitting out of the plane defined by the four ligand atoms—N,N,Cl,Cl, by 0.015(1)Å. The average bond lengths to the platinum were Pt-Cl=2.310(7)Å and Pt-N=2.04(2)Å and the bond angles around the platinum were within 86.8-92.4° (Figure 7.1). In our structure, the X-ray single crystal analysis shows that there are four *cis*-$[Pt(NH_3)_2Cl_2 \cdot (HgCl_2)_3]$ molecules in the monoclinic unit cell (Figure 7.2).

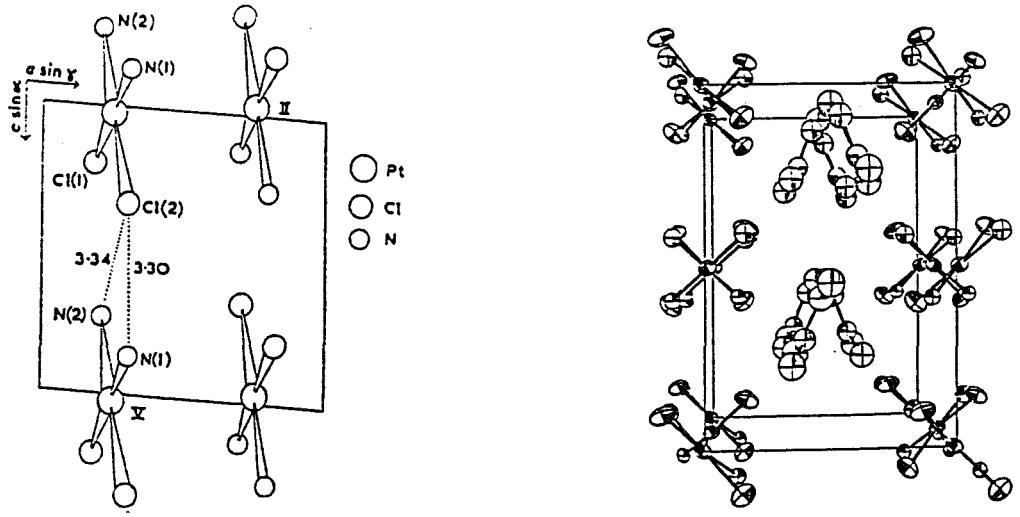


Figure 7.1 The schemes of *cis*-$[Pt(NH_3)_2Cl_2]$ and its DMF adduct

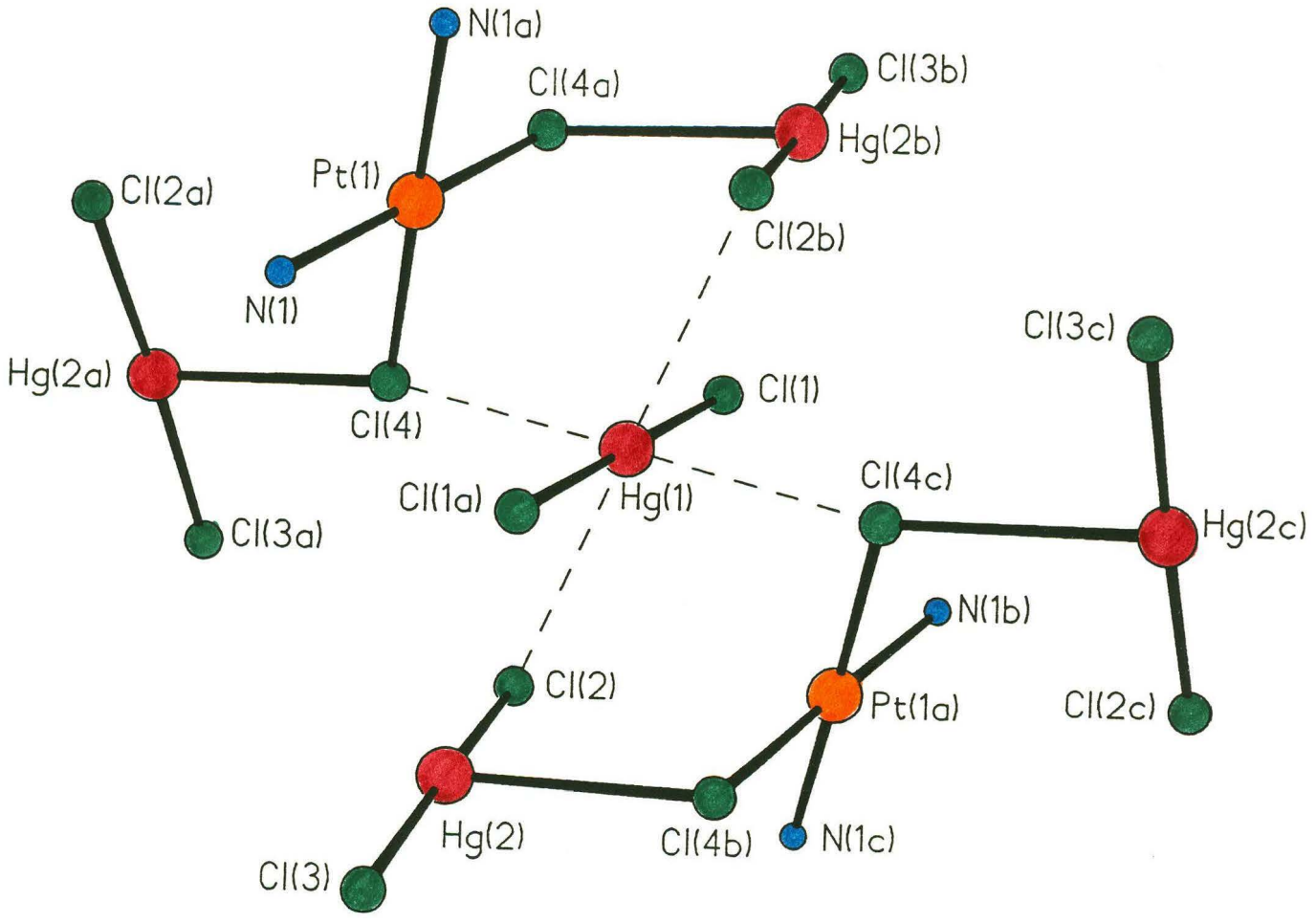


Figure 7.2 The perspective diagram of *cis*-$[Pt(NH_3)_2Cl_2 \cdot (HgCl_2)_3]$

There are two types of mercury atoms. Hg(1) is at (0,0,0) and Hg(2) in a general position. Thus Hg(1) is at the center of a perfectly linear $HgCl_2$ unit but the Cl(2)-Hg(2)-Cl(3) bond angle is 176.4(1)°. The platinum atoms lie on a two-fold axes of symmetry of special positions of type (0,y,0.25). The intramolecular distances are Hg(1)-Cl(1) 2.308(5)Å, Hg(2)-Cl(2) 2.301(5)Å, Hg(2)-Cl(3) 2.300(5)Å, Pt(1)-N(1) 2.091(2)Å, Pt(1)-Cl(4) 2.307(5)Å, Hg(1)-Cl(4) 3.004(4)Å and Hg(2)-Cl(4) 2.979(4)Å (Table 7.3). The bond angles subtended

Pt and Hg atoms range from 88.2-92.2° or 176.6-180° (Table 7.4). Compared to the uncomplexed *cis*-$Pt(NH_3)_2Cl_2$, the Pt-N bonds in this compound are elongated slightly (2.01(4) and 2.09(2)Å, respectively). The Pt-Cl bonds, on the other hand, are very similar to those found in the uncomplex *cis*-$Pt(NH_3)_2Cl_2$ [2.33(1)Å to 2.31(1)Å]. The bond angles seem only slightly changed. The Hg-Cl bonds within the $HgCl_2$ fragments are also very similar to those found in the discrete $HgCl_2$ unit [90]. The molecules are linked to each other by secondary interactions to form a polymeric structure (Figure 7.3), similar to those reported for $[Et_4N]_2Hg_2PtCl_8$ (**I**) and $[Et_4N]_2Hg_3PtCl_{10}$ (**II**) [91] (Figure 7.4).

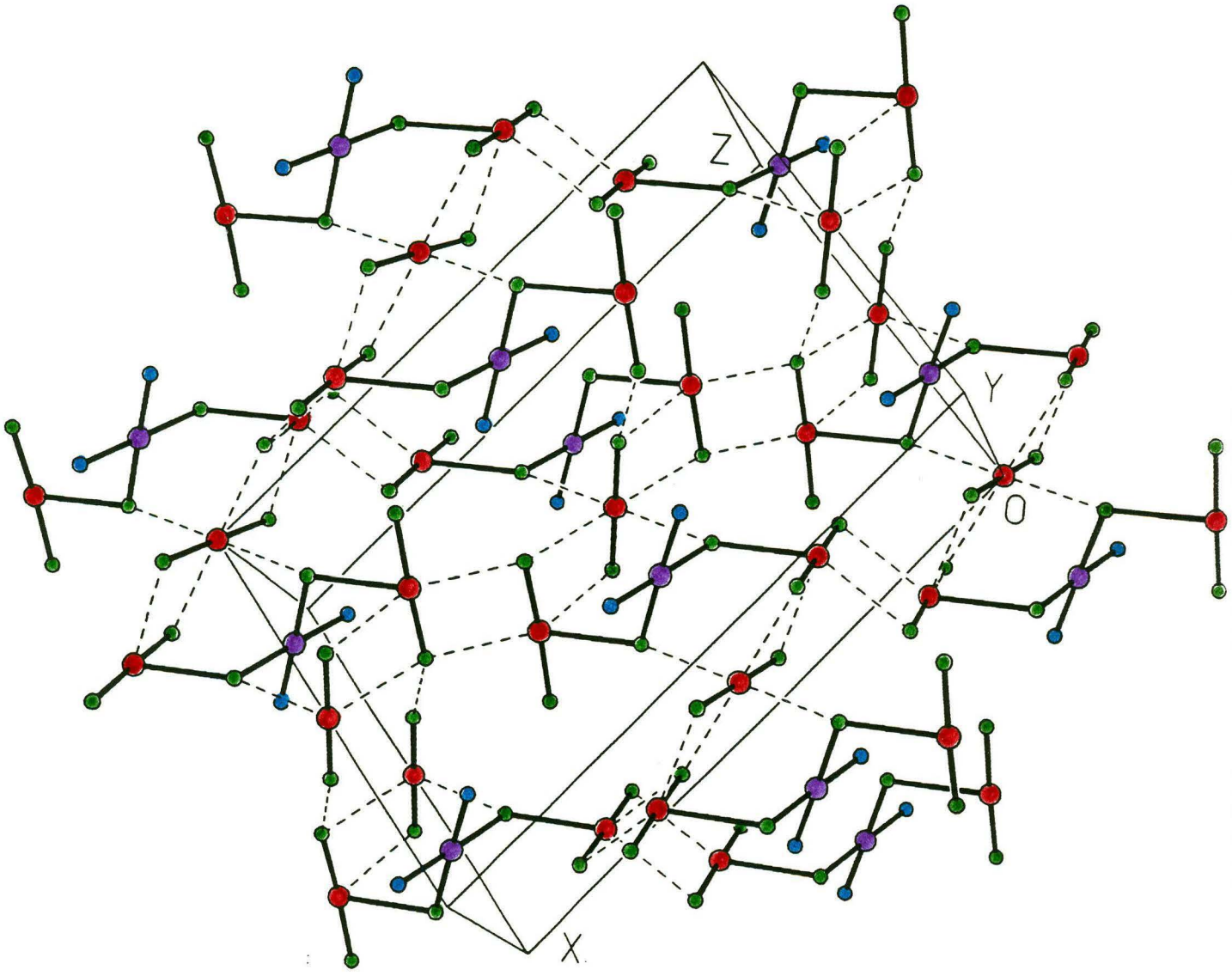


Figure 7.3 The packing diagram of $[cis\text{-}Pt(NH_3)_2Cl_2{\cdot}(HgCl_2)_3]_n$

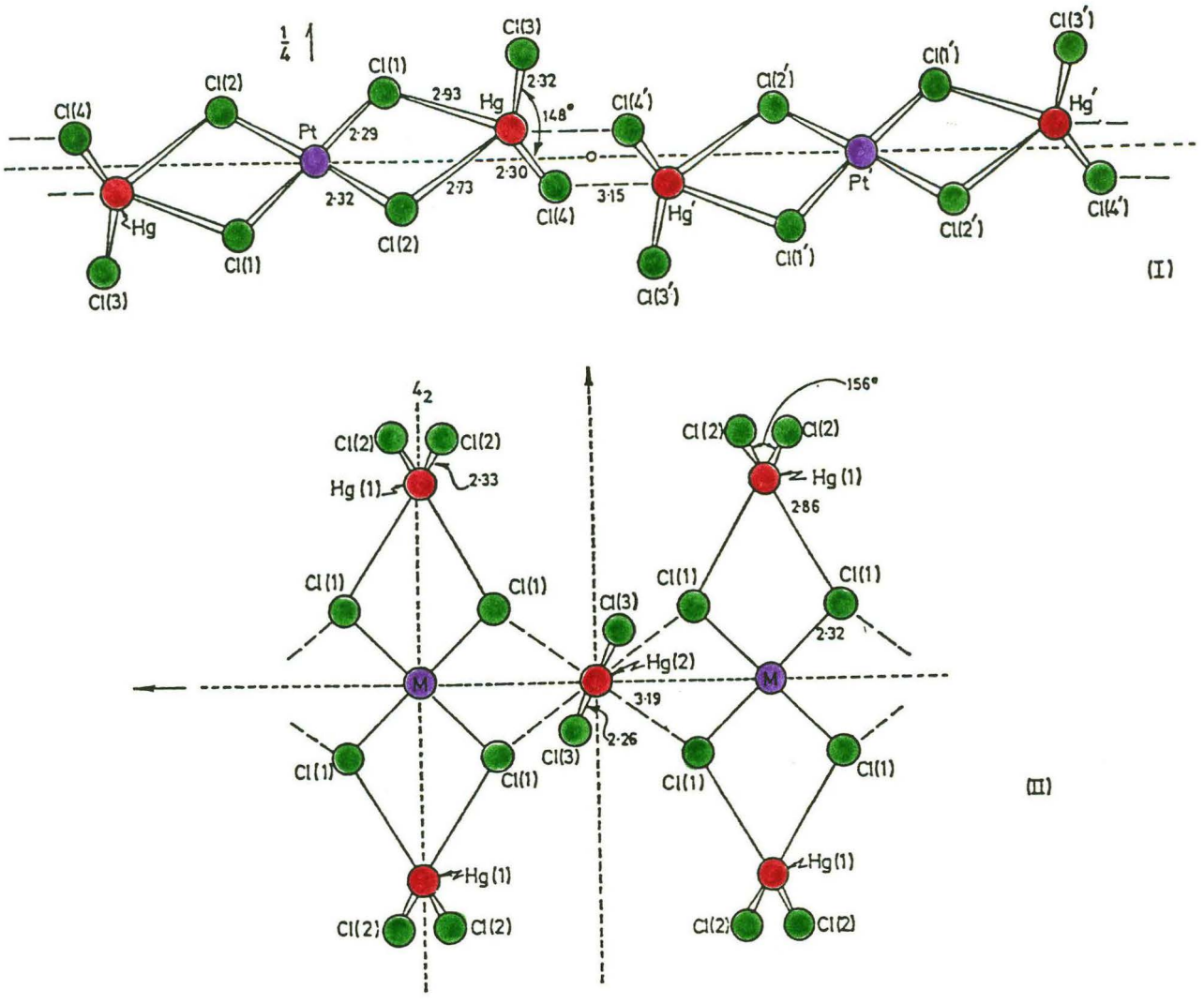


Figure 7.4 The labelling schemes of $[Et_4N]_2Hg_2PtCl_8$ (I) and $[Et_4]_2Hg_3PtCl_{10}$ (II)

In $[PtCl_2(NH_3)_2.(HgCl_2)_3]_n$, the *cis*-$PtCl_2(NH_3)_2$ units are linked into chains by bridging of the chloro ligands through the $HgCl_2$ molecule centred on a special position [Cl(4)-Hg(1)=3.004(4)Å]. The Hg atoms in this unit are also linked to Cl atoms in second $HgCl_2$ units through the secondary interactions [Hg(1)···Cl(2) 3.29Å]. The chloro ligand bound to Pt is also linked [Cl(4)-Hg(2)=2.979(4)Å] to a second $HgCl_2$ molecule, whose next closest Hg···Cl interaction is at 3.25Å from an equivalent $HgCl_2$ molecule in another chain (Figure 7.3). Thus we can regard the Hg atoms

in the first units as having approximately octahedral coordination and the chloro ligands bound to the Pt(II) as each being weakly linked to two $HgCl_2$ molecules. In the structures (I) and (II), the anions of $[Hg_3PtCl_{10}^{2-}]$ and $[Hg_2PtCl_8^{2-}]$ are also linked together through bridging chlorine atoms [Cl(1)-Hg(2)=3.19Å(I) and Hg-Cl(4)=3.15Å(II)] to form polymeric structures. In the crystal structures of chlorine compounds, a Cl···Cl distance of 3.2-3.6Å can be regarded as an non-bonding interaction[20]. Thus we consider that the Cl(1)···Cl(2) distance 3.29Å as a weak bonding interaction in our structure. The other contact (Cl(4)-Cl(3) 3.53Å) is too long to be considered as providing effective interaction.

Chapter 8

Discussion

8.1 Hg···Cl Interactions

We reviewed some of the important coordination features of mercury(II) in chapter 1 and one of these was that linear two-coordination is very common for mercury(II) and there is a tendency for the linear X-Hg-X (X=halogen) arrangement to be retained when further ligands are added [3, 5, 6, 8]. This has also been observed in most of our structural results, however, retention of the linearity of a X-Hg-X unit depends on the influence of the further ligands. Usually, the coordination sphere of mercury(II) atoms contains both close (~2.3Å) and distant but bonded atoms (>3.0Å) and everything in between. However, the coordination number rarely exceeds six and much useful systematisation can be achieved using the

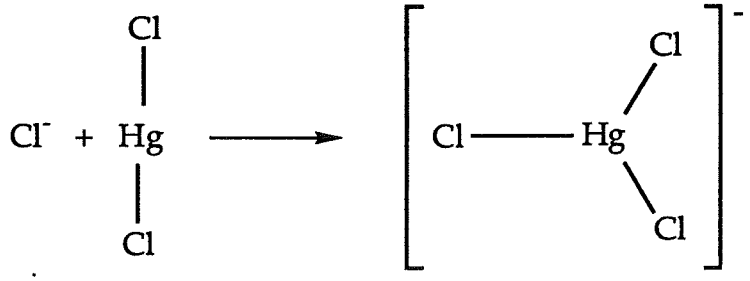
$$[2(\text{short}) + 2(\text{intermediate}) + 2(\text{long})] \equiv [2 + 2 + 2]$$

or $[2(\text{short}) + 3(\text{long}) \equiv [2 + 3]$ etc, schemes. [40, 92]

Consequently an approach based on coordination number, rather than bond length may by profitable. Nevertheless, it must be remembered that Hg(II) seems to adopt all coordination numbers from two to six, in monomers, as well as a seemingly endless variety of polymers, so even coordination number based systems will be complicated.

As we have mentioned before, the structural diversity exhibited by chloro-mercury(II) anionic systems means that a distinction between bonded and non-bonded atoms surrounding mercury(II) is not always easy. Now with a considerable quantity of crystallographic data, we are able to investigate these questions using the concept of the "Structure-correlation approach method" developed by Burgi and Dunitz [21, 22]. The principle behind this concept is that "if a correlation can be found between two or

more independent parameters describing the structure of a given structural fragment in a various environments, then the correlation function maps a minimum energy path in the corresponding parameter space."[22] It was also stated that the most remarkable aspect of the "structure-correlation approach method" was that it could be expressed as simple analytical functions derived from the assumption of bond number conservation. The structure-correlation method can be applied to the Cl-Hg-Cl + Cl^- interaction system by plotting the observed Cl-Hg-Cl bond angle against the approaching Hg-Cl distance for structural fragments containing one distorting chloro ligand (Scheme 8.1).



Scheme 8.1

Scheme 8.1 shows that when the Cl^- approaches to the neutral, linear $HgCl_2$ molecule, the two Hg-Cl bonds elongate and the Cl-Hg-Cl bond angle bends away from 180° in the opposite direction accompanied by the formation of the new Hg····Cl bond. In most of the cases it is easy to distinguish two short and one long Hg-Cl bonds and thus the distorting angle can be easily identified. For example, the $HgCl_3^-$ anion reported by Trezis, et al[94]; in this $HgCl_3^-$ structural unit, one can easily distinguish the two short Hg-Cl bonds of 2.314(3)Å and 2.315(3)Å, and one long Hg-Cl bond of 2.997(2)Å. The large angle of 178.3(1)° between the two short Hg-Cl bonds is very distinguishable too. However, when the mercury(II) atom in $HgCl_3^-$ structural fragments takes up a nearly regular trigonal coordination environment the choice of distorting angle can be quite difficult. We can

take the $HgCl_3^-$ anion, reported by Grdenic, et al [100], as an example of this case. In this $HgCl_3^-$ anion, the three Hg-Cl bonds lengths are very similar to each other (between 2.387(8)-2.421(8)Å), the bond angles are also very similar. So in this case, it would be difficult to choose the long Hg-Cl bond and the distorting angle. Figure 8.1 shows such a correlation approach diagram for a number of known $HgCl_3^-$ structural fragments (For reference data see Table 8.1). It is shown clearly in this diagram that when an approaching third chloride is further than about 3.00Å from the Hg, the interaction of this chloride with the $HgCl_2$ unit is effectively non-distorting.

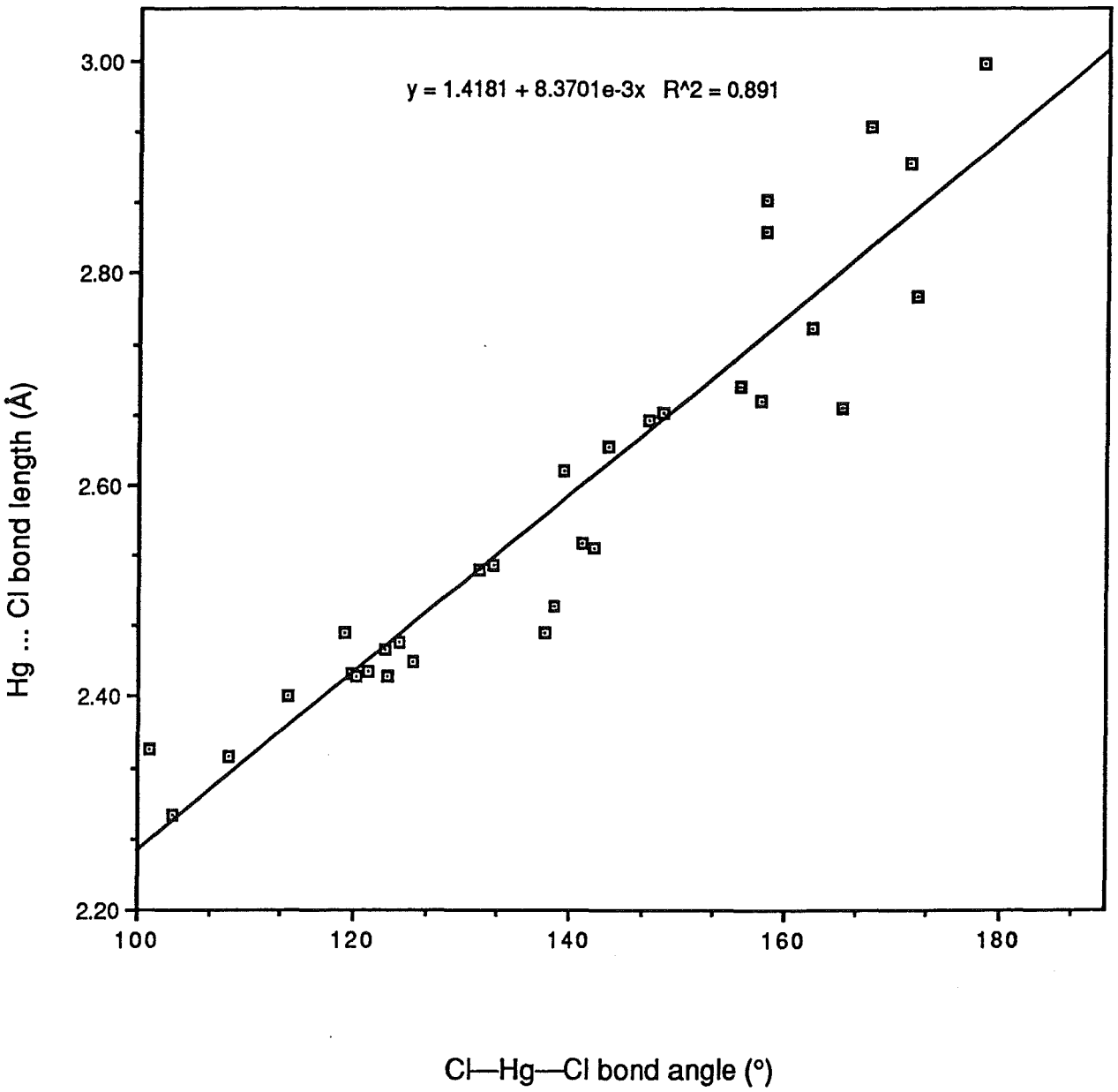

y = 1.4181 + 8.3701e-3x R^2 = 0.891
3.00
2.80
2.60
2.40
2.20
100
120
140
160
180
Hg ... Cl bond length (Å)
Cl—Hg—Cl bond angle (°)

Figure 8.1

Table 8.1 Cl-Hg-Cl(°) vs Hg····Cl(Å) in $HgCl_3^-$ fragments

Cl-Hg-Cl(°)	Hg····Cl(Å)	Reference
178.3	2.997	13
167.8	2.937	23
171.6	2.904	54
158.0	2.869	13
158.0	2.840	23
172.2	2.777	13
162.3	2.749	93
155.6	2.693	43
157.7	2.680	94
165.3	2.673	44
148.4	2.668	23
147.2	2.662	13
143.4	2.637	23
139.3	2.614	95
141.0	2.545	48
142.1	2.54	40
132.8	2.525	96
131.5	2.520	54
138.4	2.485	97
119.2	2.46	98
137.7	2.46	40
124.2	2.451	14
122.9	2.444	42
125.5	2.434	99
121.2	2.425	100
119.7	2.421	100
120.2	2.42	40
123.0	2.42	98
114.0	2.40	40
101.0	2.35	40
108.4	2.345	97
103.2	2.29	40

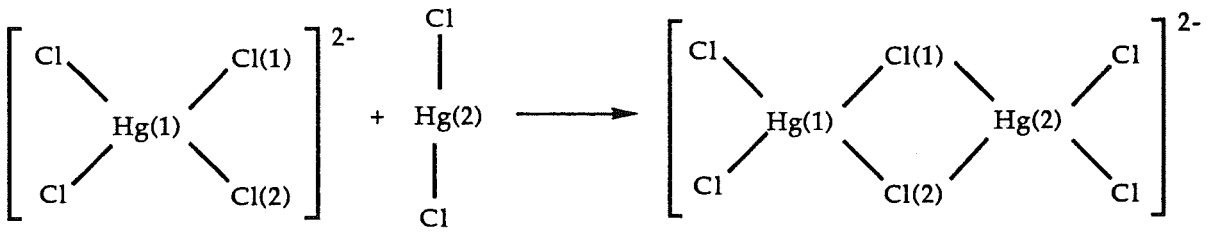
Ben Salah, et al [23], have attempted a similar structure-correlation process by using

$$HgCl_2 + 2Cl^- \rightarrow HgCl_4^{2-}$$

and $$HgCl_2 + 4Cl^- \rightarrow HgCl_6^{4-}$$

systems where the average of the two longer Hg-Cl bonds is plotted against the average of the two shorter bonds. However their plot is considerably scattered and is distinctly curved as well. We think this is because under the influence of two or more free chloride ions, the system has become very complicated as the interactions among these reactants are very unpredictable.

From our analyses, we believe that the structure-correlation method provides an effective way to determine the coordination sphere and numbers. We can apply another similar analysis to the distinctions in $Hg_2Cl_6^{2-}$ units, here using our results and available crystallographic data. These $Hg_2Cl_6^{2-}$ units (structural fragments) can be formally regarded as products along the reaction path shown in Scheme 8.2. It shows that when Cl(1) and Cl(2) approach the Hg(2), the Cl-Hg(2)-Cl bond angle starts bending away and the two Hg(2)-Cl bonds elongate, forming an $Hg_2Cl_6^{2-}$ unit.



Scheme 8.2

The majority of $Hg_2Cl_6^{2-}$ units have unequal lengths of Hg-Cl bridging bonds and Hg-Cl terminal bonds. The resulting plot is shown in Figure 8.2 (For reference data see Table 8.2), the two Hg-Cl bridging bond lengths are plotted against the Cl-Hg-Cl terminal bond angle.

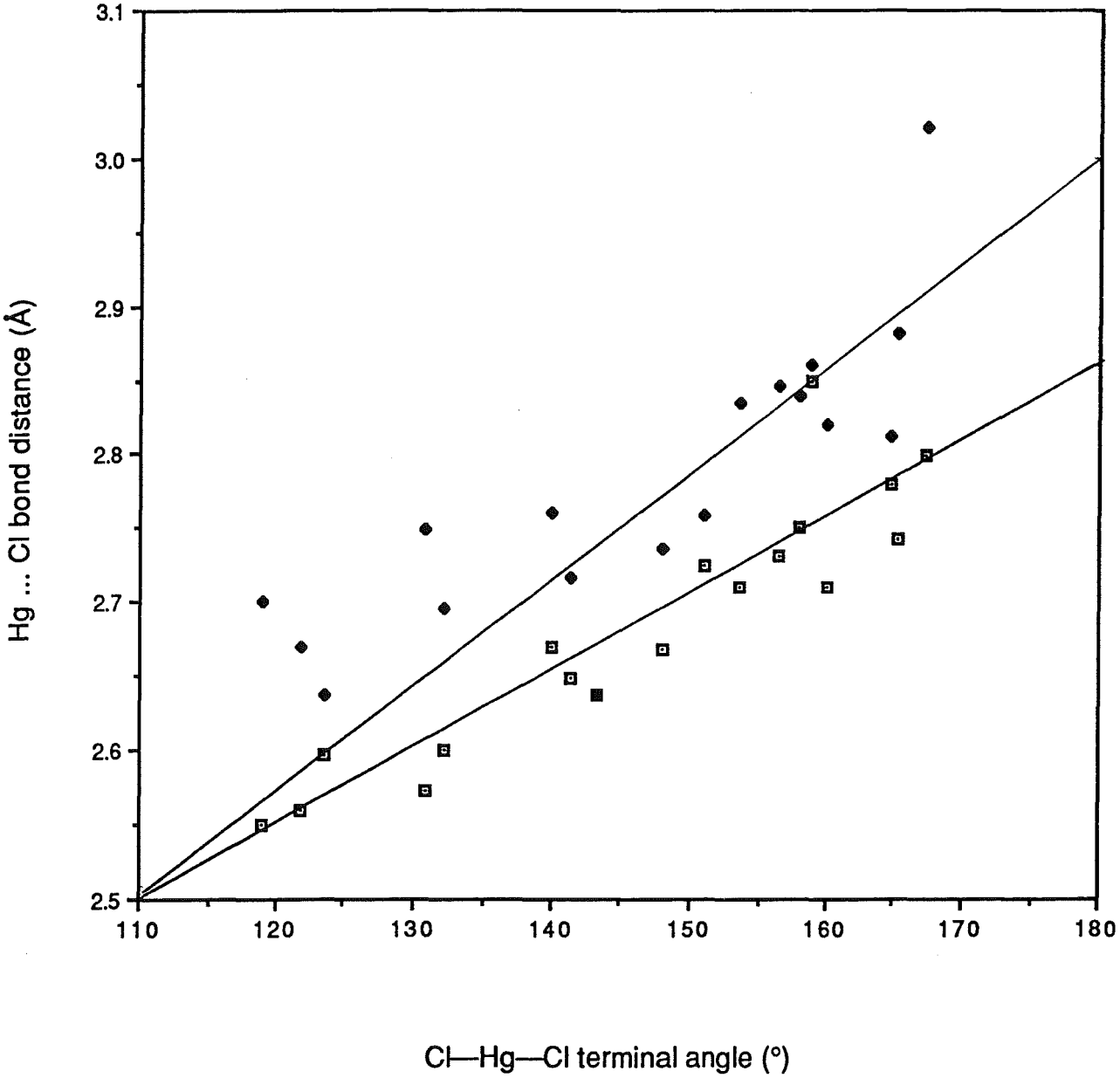

3.1
3.0
2.9
2.8
2.7
2.6
2.5
Hg ... Cl bond distance (Å)
110
120
130
140
150
160
170
180
Cl—Hg—Cl terminal angle (°)

Figure 8.2

Table 8.2 Cl-Hg-Cl terminal angle in $HgCl_2$ units vs Hg-Cl···Hg bridging distance

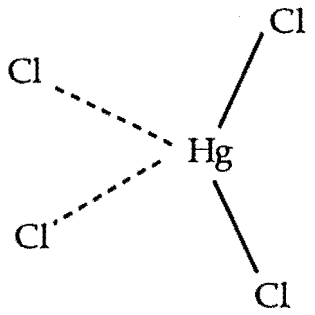
Cl-Hg-Cl(°)	Hg-Cl bridging distance(Å)		Reference
	short	long	
167.3	2.80	3.02	40
165.2	2.742	2.881	44
164.7	2.780	2.812	101
160	2.71	2.82	102
158.8	2.85	2.86	40
158.0	2.750	2.840	54
156.5	2.732	2.846	54
153.6	2.710	2.835	103
151.1	2.725	2.759	44
148.0	2.668	2.736	54
143.3	2.637	2.637	23
141.3	2.648	2.717	49
140.0	2.67	2.76	104
132.2	2.60	2.696	48
130.9	2.572	2.749	101
123.6	2.597	2.638	104
121.9	2.56	2.67	50
119	2.55	2.70	104

Again it shows that when the approaching Hg···Cl distance is greater than about 3.00Å, the approaching chloride ion has no effect on the Cl-Hg-Cl bond angle. Thus we conclude, here, from our analytical results for these few different systems, that when the distance to an approaching chloride is as close as about 3.00Å, the influence of this chloride on a $HgCl_2$ molecule is strong enough to cause bending of the Cl-Hg-Cl bond angle away from 180°.

Now we have defined that 3.00Å is the upper limit for an approaching chloride ion to distort an $HgCl_2$ unit. However, when Hg-Cl distance is slightly greater than 3.00Å we believe that there is still an interaction between the mercury(II) and chloride ions. So another question arises here.

That is how we determine whether an Hg···Cl interaction as an effective interaction or a non-effective interaction and how we determine the "effective coordination number" for a mercury atom (which is defined as the number of the neighbouring atoms, within a distance of the sum of the van der Waals radii of the interacting atoms). In this particular case, it means the number of the approaching chlorides within the distance of the sum of the van der Waals radii of mercury and chlorine atoms. The precise value of the sum of the van der Waals radii for mercury and chlorine atoms has been a very confusing question in chloro-mercury(II) studies and, as we have mentioned before, different researchers define it differently. Grdenic[8] proposed the value of 1.73Å as the van der Waals radius for mercury atom in his early review thus the sum of the van der Waals radii for mercury and chlorine would be (1.73+1.80)=3.53Å. However in one of his later reviews [119] he suggested to use 1.55Å as the van der Waals radius for mercury atom according to the number of available crystallographic data. Kuzmina and Struchkov[3] introduced the concept of "Secondary interaction" and they tended to adopt the minimal value of 1.5-1.6Å as the van der Waals radius for mercury thus the sum of the van der Waals radii for Hg···Cl would in the range of 3.35-3.45Å. In a review paper, Larock, et al [40], used the value of 3.30Å as the sum of the van der Waals radii for the mercury and chlorine atoms. In our study we adopt the average minimal values of 1.55Å as the van der Waals radius for mercury atom and the value of 1.80Å as the van der Waals radius for chlorine atom thus we consider that the sum of the van der Waals radii for the mercury and chlorine atoms is up to 3.35Å. This value 3.35Å has been used as the upper limit for Hg···Cl interaction through all of our study and discussion. We have also considered, according to the definition of the "effective interaction", that if a distance of an Hg···Cl interaction is within 3.35Å, it is regarded as an effective interaction.

However we still have occasional difficulty in describing some structural fragments, such as $HgCl_4^{2-}$. Should we describe them as distorted $HgCl_4^{2-}$ units or should we describe them as linear $HgCl_2$ molecules distorted by the close approach of the two chloride ions? (Scheme 8.3)



Scheme 8.3

To clarify this point, a plot of the mean Hg···Cl bond lengths against the Cl-Hg-Cl bond angle for a number of known examples has been carried out and the result is shown in Figure 8.3 (For reference data see Table 8.3). Once again it shows that at a distance of less than 3.00Å, a Hg-Cl bond is formed and the structural unit $HgCl_4^{2-}$ is best described as a distorted $HgCl_4^{2-}$ species.

Table 8.3 Data for $2Cl^- + HgCl_2$ interactions

	Angle(°)	Hg-Cl(Å)		Hg-Cl(Å)(mean)	Ref.
$[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$	175.9	2.95	3.07	3.01	51
$[H_3dpt]_2[Hg_3Cl_{12}]$	172.6	2.81	3.08	2.95	76
$[Me_2NH_2][Hg_2Cl_5]$	171.6	2.90	2.97	2.94	54
	162.0	2.80	2.76	2.78	54
$[H_2en][HgCl_3]$	165.1	2.75	2.81	2.78	76
$[MeNH_3][HgCl_3]$	160.1	2.71	2.82	2.77	102
	157.7	2.68	2.86	2.77	43
$[Me_2NH_2][HgCl_3]$	156.5	2.73	2.85	2.79	54
	148.4	2.67	2.74	2.70	54
$[Me_3NH][HgCl_3]$	143.3	2.64	2.64	2.64	23

We would consider usually, according to our analytical data and the experimental results, that at a distance less than ~3.10Å, Hg-Cl bonds formed and the approaching chloride ions are regarded as part of the Hg(II) structural unit.

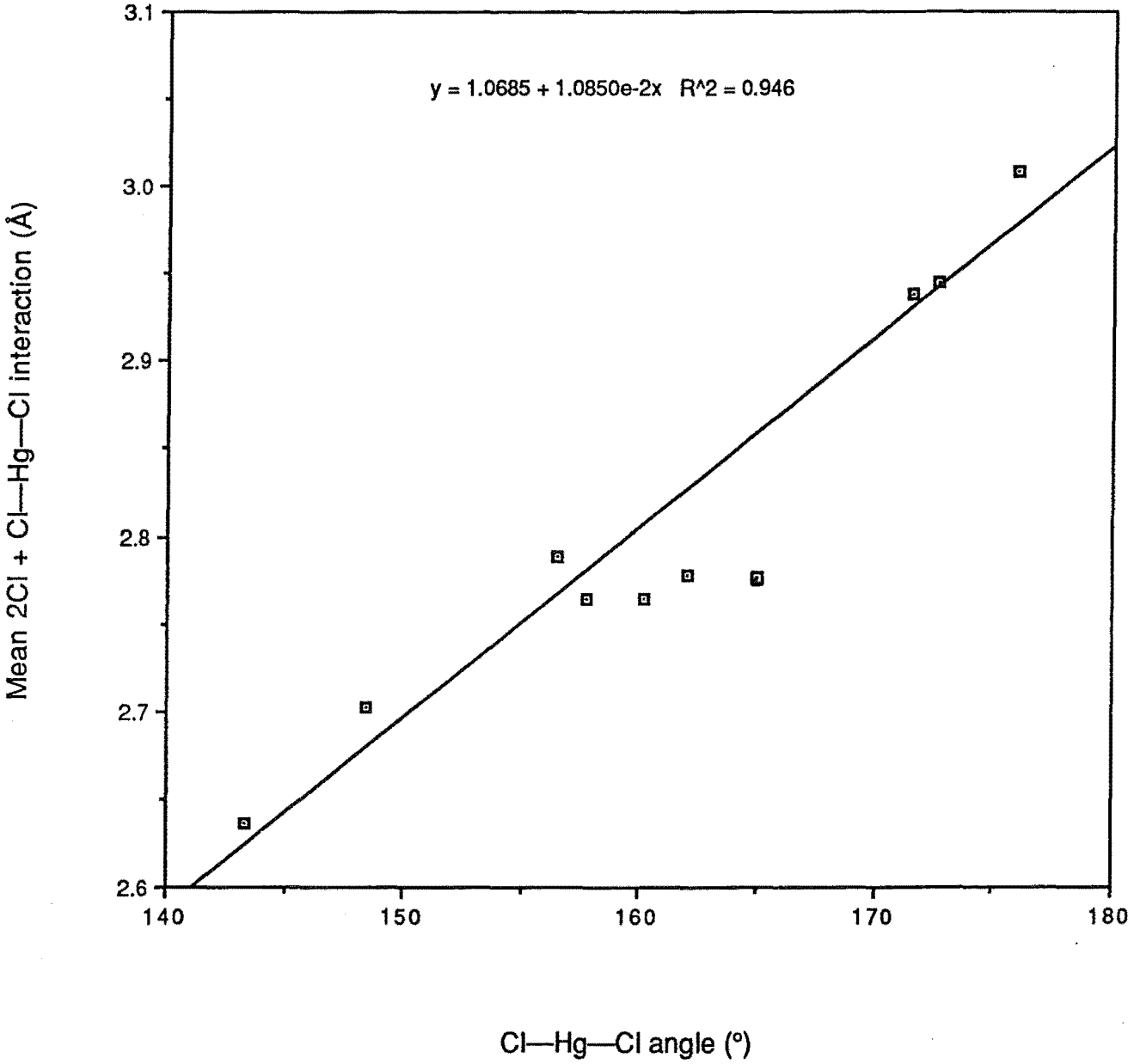

y = 1.0685 + 1.0850e-2x R^2 = 0.946
Mean 2Cl + Cl—Hg—Cl interaction (Å)
Cl—Hg—Cl angle (°)
3.1
3.0
2.9
2.8
2.7
2.6
140
150
160
170
180

Figure 8.3

8.2 Hydrogen Bonding and Cl···Cl Interactions

Table 8.4 Hydrogen Bonding

Compounnd	N-H···Cl(O) (Å)	H···Cl(O) (Å)	N-H···Cl(O) (°)
$(H_2en)_2(HgCl_4)(Cl)_2$			
N(1)-H(1A)···Cl(2)	3.17	2.36	151
N(1)-H(1B)···Cl(1)	3.23	2.24	163
N(1)-H(1C)···Cl(4)	3.56	2.36	152
N(2)-H(2A)···Cl(4)	3.18	2.28	159
N(2)-H(2B)···Cl(4)	3.15	2.23	160
N(2)-H(2C)···Cl(4)	3.19	2.35	145
$(H_2en)(Hg_2Cl_6)$			
N(1)-H(1A)···Cl(3)	3.23	2.42	142
N(1)-H(1B)···Cl(1)	3.25	2.51	139
$(H_4trien)(Hg_2Cl_8)$			
N(2)-H(2B)···Cl(8)	3.18	2.28	155
N(2)-H(2A)···Cl(5)	3.22	2.32	157
N(4)-H(4D)···Cl(5)	3.16	2.27	155
N(4)-H(4C)···Cl(1)	3.26	2.38	152
N(4)-H(4E)···Cl(1)	3.30	2.41	154
N(1)-H(1E)···Cl(8)	3.19	2.24	168
N(1)-H(1C)···Cl(8)	3.29	2.39	157
N(3)-H(3C)···Cl(3)	3.08	2.16	160
N(3)-H(3D)···Cl(6)	3.18	2.35	145
***trans*-$[Co(en)_2Cl_2]_2[Hg_2Cl_6]$**			
N(1)-H(1B)···Cl(4)	3.34	2.48	149
N(2)-H(2B)···Cl(2)	3.32	2.50	143
$[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$			
N(1)-H(1A)···Cl(4)	3.39	2.44	168
N(2)-H(2B)···Cl(1)	3.47	2.57	166
N(2)-H(2C)···O(1)	2.97	2.43	116
N(3)-H(3A)···Cl(7)	3.36	2.48	152
N(3)-H(3C)···Cl(5)	3.36	2.41	132
N(5)-H(5A)···Cl(4)	3.31	2.42	151
***cis*-$[PtCl_2(NH_3)_2\cdot(HgCl_2)_3]$**			
N(1)-H(1B)···Cl(1)	3.39	2.61	147
N(1)-H(1A)···Cl(4)	3.46	2.63	144

Hydrogen bonding has been found to exist in most of our structures (Table 8.4). The H····Cl contact distances range from 2.16-2.63Å, which correspond with strong (H····Cl<2.2Å), medium-strong (2.3-2.4Å) and weak (2.5-2.6Å) hydrogen bonding, in our structures. This distance range is about 0.7-0.2Å shorter than the sum of the van der Waals radii of hydrogen and chlorine atoms. These hydrogen bonds do not affect the formation of cations and anions in the structures but these weak electrostatic interactions may be important in determining some of the packing characteristics of these crystal structures.

Some Cl···Cl long interactions have also been found in the crystal structure of two compounds: $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$ and *cis*-$[PtCl_2(NH_3)_2\cdot(HgCl_2)_3]$ (Table 8.5).

Table 8.5 The Cl···Cl interactions

Compound	Cl···Cl(Å)
$[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$	
Cl(7)···Cl(9)	3.38
Cl(3)···Cl(5)	3.39
***cis*-$[PtCl_2(NH_3)_2\cdot(HgCl_2)_3]$**	
Cl(1)···Cl(2)	3.29
Cl(4)···Cl(4)	3.31

There is much evidence that Cl atoms in many molecular solids do not function as groups of a certain volume (close packing) but rather through specific anisotropic, electronic effects, according to Desiraju, et al [20]. So the Cl···Cl contacts must be attractive and directional. This has been inferred from a study of a number of crystal structures [124]. Through these Cl···Cl interactions additional stabilization seems to be achieved in the packing arrangement of these crystal structures. So we conclude that these long

Cl···Cl contacts play the similar role as hydrogen bonds in the packing of these crystal structures.

8.3 The Integrity of These Chloro-mercury(II) Anions in Solution

What sort of stability do chloro-mercury(II) ions have in solution? This question has often been asked but the answer is not forthcoming. A few reviews[121-123] are available with speculative conclusions.

The main reason for lack of progress in this area is that we are still lacking sophisticated enough equipment to detect the behaviour of these chloro-mercury(II) clusters in solution. Also the factors that cause these chloro-mercury(II) anions form monomers, dimers or polymers in crystals is unknown yet.

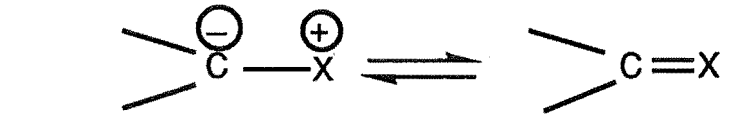
Of the techniques available, ^{199}Hg nmr.[125], ion chromatography or ion electrophoresis may be useful but the work remains to be done.

Chapter 9

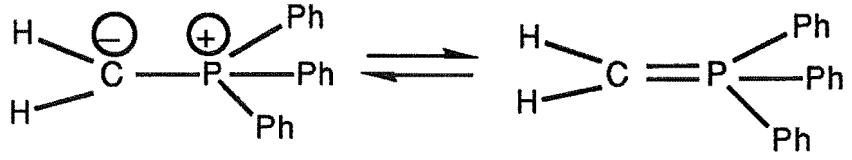
Crystal Structure of $(Ph_3P)CHCOPh$ and Its Complexes with $HgCl_2$ and HgI_2

9.1 Introduction

The title organophosphorus compound belongs to the general class of molecules known as ylides. An ylide can be defined as a compound in which a carbanion is attached directly to a heteroatom carrying a high degree of positive charge [105]:



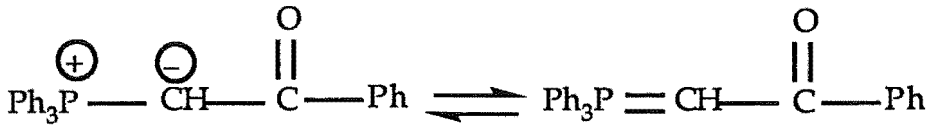
eg.



(1a) (1b)

Scheme 9.1

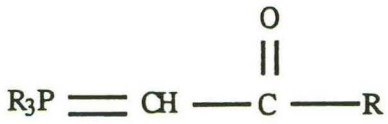
Consequently the formal structure of the title ligand is:



(triphenylphosphinebenzoylmethylene or triphenylphenacylidenephosphorane)[106]

Scheme 9.2

This class of P ylide (or phosphorane) is more stable than the methylide(1), as more extensive electron delocalization can occur over the skeleton of:



Scheme 9.3

Typical bond lengths in methylides are P=C 1.66Å and P-Ph 1.81Å [107], respectively. The P=C bond length of about 1.76Å in a phosphorane stablized by two electron-withdrawing carbonyl groups (Figure 9.1) [108], is considerably longer than the equivalent bond length of 1.66Å for the non-stablized phosphorane.

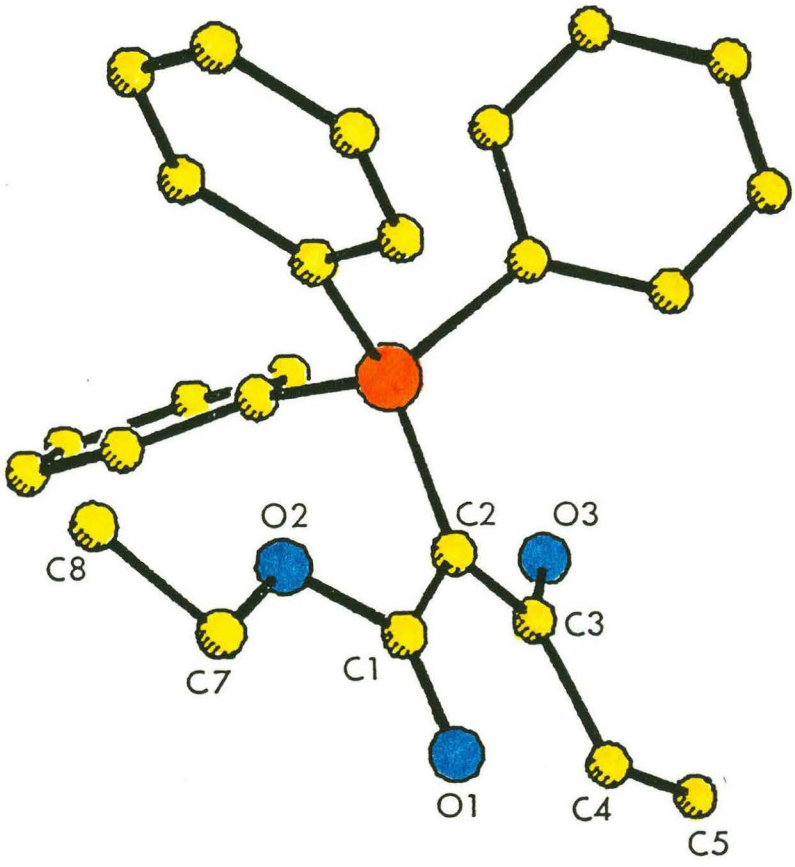
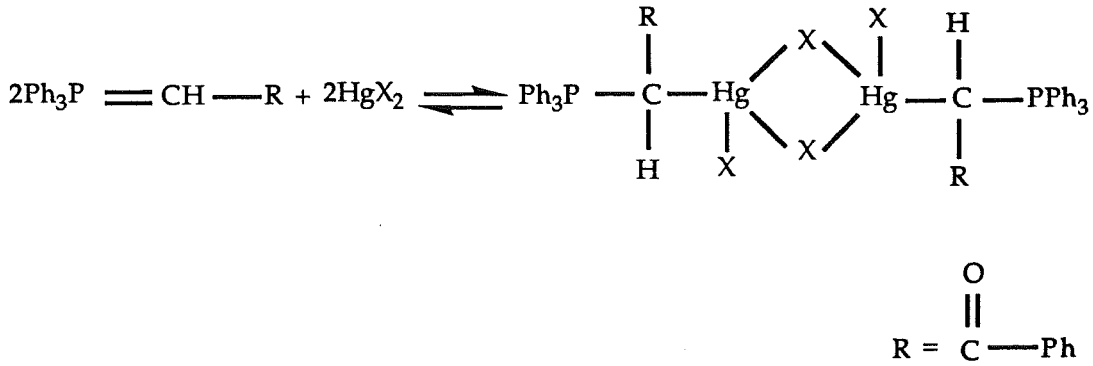


Figure 9.1 The diagram of a phosphorane stablized by two electron-withdrawing carbonyl groups

It is of interest to see how these distances change as the delocalization systems are changed. The title compound also forms adducts with $HgCl_2$ and HgI_2 and the structure of these compounds reveals the formation of an Hg-C bond from the formal opening of the Ph_3P=C- double bond.

Adduct Formation:



Scheme 9.4

$[(Ph_3P)CHCOPh{\cdot}HgCl_2]{\cdot}CH_3OH$ and $[(Ph_3P)CHCOPh{\cdot}HgI_2]$ are two examples of a small number of organomercury compounds with a non-linear distorted tetrahedral coordination of the Hg atom. As part of our investigations on the structural complexity of mercury(II) halide anions, we report here the X-ray structures of $(Ph_3P)CHCOPh$, $[(Ph_3P)CHCOPh{\cdot}HgCl_2]{\cdot}CH_3OH$ and $[(Ph_3P)CHCOPh{\cdot}HgI_2]$.

9.2 X-ray Crystal Structure Determinations

Crystals of these three compounds were provided by Dr. Panchanatheswaran, Department of Chemistry, Bharathidasan University, Tiruchirapalli, India.

Crystal data for the three compounds are listed in Table 9.1. Intensity data were collected with a Nicolet R3m four-circle diffractometer at -120°C. Graphite monochromated MoKα radiation (λ=0.71069Å) was used, with fixed speed omega scans for $[(Ph_3P)CHCOPh{\cdot}HgCl_2]{\cdot}CH_3OH$ and $[(Ph_3P)CHCOPh{\cdot}HgI_2]$ and peak top Wyckoff scans for $(Ph_3P)CHCOPh$.

Table 9.1. Crystal Data

Complex	$[(Ph_3P)CHCOPH]_2$ (1)	$[(Ph_3P)CHCOPh{\cdot}HgCl_2]_2{\cdot}2CH_3OH$ (2)	$[(Ph_3P)CHCOPh{\cdot}HgI_2]_2$ (3)
Molecular formula	$C_{26}H_{21}OP$	$C_{54}H_{50}O_4P_2Cl_4Hg_2$	$C_{26}H_{21}OPI_2Hg$
Formula weight	380	1367	834
Crystal size (mm)	0.18x0.38x0.42	0.06x0.09x0.30	0.10x0.18x0.42
Space group	monoclinic P2/n	triclinic $P\bar{1}$	hexgonal $R\bar{3}$
a(Å)	18.9778(7)	10.485(5)	36.664(9)
b(Å)	10.9123(5)	10.142(3)	36.664(9)
c(Å)	19.6198(11)	14.115(4)	10.589(3)
α(°)	90	76.60(2)	90
β(°)	105.01(4)	64.11(3)	90
γ(°)	90	68.08(3)	120
V(Å^3)	3952(3)	1248(1)	12328(7)
Z	8	1	18
$D_{calc(g/cc)}$	1.28	1.80	2.02
Temperature(K)	153	153	153
F(000)	1600	656	6947
Linear absorption coefficient (cm^{-1})	1.48	64.62	79.20
Transmission factors	0.775	0.734	0.571
	0.785	0.986	0.953
Merge	0.022	0.023	0.016
Scan mode	Wycoff	omega	omega
Octants	h, k, ±l	h, ±k, ±l	h, k, ±l

Continued...

$2\theta_{max}(°)$	52	50	52
Reflections measured	7758	4407	5391
Reflections used	3140	3734	3136
Parameters refined	409	202	102
Weighting ($gx10^3$)	0.0	7.2	2.6
GOOF	1.63	1.32	1.06
R	6.22	3.67	4.12
R_w	4.69	3.74	3.75

The structures of $[(Ph_3P)CHCOPh{\cdot}HgCl_2]{\cdot}CH_3OH$ (2) and $[(Ph_3P)CHCOPh{\cdot}HgI_2]$ (3) were solved by conventional Patterson and Fourier methods and refined by blocked cascade least-squares procedures but direct methods were used to solve the structure of $(Ph_3P)CHCOPh$(1). For structures (2) and (3), only Hg, Cl(1) and P atoms were refined with anisotropic thermal parameters, but for structure (1) satisfactory refinement was obtained with anisotropic thermal parameters for all non-hydrogen atoms. For structures (1), (2) and (3), the carbon atoms inside the phenyl groups were refined using a rigid model. Hydrogen atoms were inserted at calculated positions using a riding model with fixed thermal parameters. The final Fourier showed no significant peaks left for structure (1) (the maximum peak 0.36eÅ^{-3} and the largest hole -0.36eÅ^{-3}). The maximum peak and the largest hole are 2.51eÅ^{-3} and -2.14eÅ^{-3} for structure (2) and 1.05eÅ^{-3} and -0.97eÅ^{-3} for structure (3), respectively.

Tables 9.2–9.4 list the non-hydrogen atom coordinates, bond lengths and bond angles for structure (1), tables 9.5–9.7 for structure (2) and tables 9.8–9.10 for structure (3).

for [(Ph3P)CHCOPh]

Table 9.2 Atomic coordinates (x10^4) and equivalent isotropic displacement coefficients (Å^{2}x10^3)

	x	y	z	U(eq)
P(1)	1535(1)	-31(2)	775(1)	18(1)
P(1')	5679(1)	5513(2)	1474(1)	17(1)
O(1)	2005(2)	819(4)	-419(2)	26(2)
O(1')	4509(2)	3904(4)	1875(2)	26(2)
C(1)	1273(3)	-643(5)	-58(3)	18(2)
C(2)	1569(3)	-74(6)	-564(3)	19(2)
C(1')	4740(3)	5579(5)	1215(3)	16(2)
C(2')	4292(3)	4771(5)	1463(3)	20(2)
C(11)	435(2)	-1047(3)	1269(2)	32(3)
C(12)	130	-1877	1652	38(3)
C(13)	577	-2695	2115	36(3)
C(14)	1330	-2683	2196	35(3)
C(15)	1634	-1852	1813	32(3)
C(16)	1187	-1034	1350	20(2)
C(21)	765(2)	-1302(3)	-1570(2)	27(3)
C(22)	566	-1647	-2279	26(2)
C(23)	964	-1221	-2737	25(2)
C(24)	1561	-449	-2486	28(2)
C(25)	1759	-104	-1778	22(2)
C(26)	1362	-530	-1320	17(2)

Continued...

Continued...

C(21')	3172(2)	5698(3)	608(2)	22(2)
C(22')	2424	5937	420	28(3)
C(23')	1984	5480	831	30(2)
C(24')	2292	4785	1431	33(3)
C(25')	3040	4546	1619	29(3)
C(26')	3479	5003	1208	17(2)
C(45')	6492(2)	6723(3)	2686(2)	34(3)
C(44')	6772	6845	3413	46(3)
C(43')	6646	5933	3866	34(3)
C(42')	6239	4899	3590	42(3)
C(41')	5959	4777	2862	38(3)
C(46')	6085	5689	2410	18(2)
C(11')	5710(2)	7937(4)	1101(2)	24(2)
C(12')	5886	8920	722	29(3)
C(13')	6322	8733	258	28(3)
C(14')	6582	7563	173	29(3)
C(15')	6406	6580	552	26(2)
C(16')	5970	6767	1016	15(2)
C(35')	5654(1)	3357(3)	715(2)	20(2)
C(34')	5973	2334	490	21(2)
C(33')	6711	2084	779	28(3)
C(32')	7130	2857	1293	27(3)
C(31')	6812	3880	1517	23(2)
C(36')	6073	4130	1228	16(2)
C(31)	1127(2)	1892(3)	1537(2)	25(2)
C(32)	783	3002	1594	27(3)
C(33)	477	3689	991	32(3)
C(34)	515	3267	330	32(3)
C(35)	858	2156	273	26(3)
C(36)	1164	1469	876	19(2)
C(41)	2911(2)	-1000(3)	1047(2)	23(2)
C(42)	3671	-986	1279	24(2)
C(43)	4033	84	1561	29(2)
C(44)	3635	1140	1611	25(2)
C(45)	2875	1125	1378	21(2)
C(46)	2513	55	1096	20(2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 9.3 Bond lengths (Å)

P(1)-C(1)	1.716 (5)	P(1)-C(16)	1.815 (4)
P(1)-C(36)	1.814 (4)	P(1)-C(46)	1.801 (4)
P(1')-C(1')	1.723 (5)	P(1')-C(46')	1.808 (4)
P(1')-C(16')	1.801 (4)	P(1')-C(36')	1.806 (4)
O(1)-C(2)	1.263 (7)	O(1')-C(2')	1.244 (7)
C(1)-C(2)	1.406 (8)	C(2)-C(26)	1.517 (6)
C(1')-C(2')	1.398 (8)	C(2')-C(26')	1.514 (6)

Table 9.4 Bond angles (°)

C(1)-P(1)-C(16)	107.1(2)	C(1)-P(1)-C(36)	115.5(2)
C(16)-P(1)-C(36)	105.2(2)	C(1)-P(1)-C(46)	111.9(2)
C(16)-P(1)-C(46)	108.8(2)	C(36)-P(1)-C(46)	108.0(2)
C(1')-P(1')-C(46')	115.6(2)	C(1')-P(1')-C(16')	104.4(2)
C(46')-P(1')-C(16')	108.7(2)	C(1')-P(1')-C(36')	115.1(2)
C(46')-P(1')-C(36')	105.2(2)	C(16')-P(1')-C(36')	107.5(2)
P(1)-C(1)-C(2)	115.4(4)	O(1)-C(2)-C(1)	122.7(5)
O(1)-C(2)-C(26)	117.6(5)	C(1)-C(2)-C(26)	119.7(5)
P(1')-C(1')-C(2')	123.1(4)	O(1')-C(2')-C(1')	125.3(5)
O(1')-C(2')-C(26')	118.7(5)	C(1')-C(2')-C(26')	116.0(4)
P(1)-C(16)-C(11)	117.5(1)	P(1)-C(16)-C(15)	122.2(1)
C(2)-C(26)-C(21)	121.6(3)	C(2)-C(26)-C(25)	118.3(3)
C(2')-C(26')-C(21')	122.5(3)	C(2')-C(26')-C(25')	117.4(3)
P(1')-C(46')-C(45')	121.8(1)	P(1')-C(46')-C(41')	118.1(1)
P(1')-C(16')-C(11')	118.2(1)	P(1')-C(16')-C(15')	121.7(1)
P(1')-C(36')-C(35')	120.0(1)	P(1')-C(36')-C(31')	119.8(1)
P(1)-C(36)-C(31)	121.0(1)	P(1)-C(36)-C(35)	118.8(1)
P(1)-C(46)-C(41)	117.4(1)	P(1)-C(46)-C(45)	122.6(1)

for $[(Ph_3P)CHCOPh \cdot HgCl_2] \cdot CH_3OH$

Table 9.5 Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2 x10^3$)

	x	y	z	U(eq)
Hg(1)	-1743(1)	250(1)	1273(1)	23(1)
Cl(1)	-957(2)	1584(2)	-698(1)	22(1)
Cl(2)	-2964(2)	-1236(3)	1105(2)	36(1)
O(1)	-4652(5)	2217(5)	3377(4)	23(2)
C(11)	1425(5)	956(5)	1851(3)	22(2)
C(12)	2839	1084	1521	23(2)
C(13)	3191	1564	2200	23(2)
C(14)	2128	1915	3207	24(2)
C(15)	714	1787	3537	21(2)
C(16)	362	1307	2859	15(1)
C(21)	33(4)	-1763(4)	3650(4)	18(1)
C(22)	148	-3207	3890	25(2)
C(23)	-1050	-3656	4071	28(2)
C(24)	-2365	-2663	4013	27(2)
C(25)	-2481	-1219	3773	22(2)
C(26)	-1282	-769	3591	15(1)
C(31)	-3271(5)	1185(3)	5426(3)	20(1)
C(32)	-4125	1839	6372	24(2)
C(33)	-4354	3281	6388	23(2)
C(34)	-3729	4070	5458	24(2)
C(35)	-2875	3417	4512	21(2)
C(36)	-2646	1974	4496	18(1)
C(41)	-3318(3)	4567(5)	1043(3)	23(2)
C(42)	-3883	5807	485	26(2)
C(43)	-5421	6416	772	26(2)
C(44)	-6393	5784	1619	25(2)
C(45)	-5828	4544	2177	20(1)
C(46)	-4291	3936	1889	17(1)
C(1)	-2103(7)	1900(7)	2230(5)	17(3)
C(2)	-3756(7)	2648(7)	2570(5)	16(3)
P(1)	-1463(2)	1108(2)	3288(1)	14(1)
O(2)	-1597(7)	5352(8)	2144(5)	51(4)
C(3)	-44(11)	5001(10)	1537(8)	50(5)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 9.6 Bond lengths (Å)

Hg(1)-Cl(1)	2.709 (2)	Hg(1)-Cl(2)	2.416 (3)
Hg(1)-C(1)	2.214 (9)	Hg(1)-Cl(1A)	2.625 (2)
Cl(1)-Hg(1A)	2.625 (2)	O(1)-C(2)	1.229 (8)
C(16)-P(1)	1.813 (6)	C(26)-P(1)	1.808 (5)
C(36)-P(1)	1.803 (4)	C(46)-C(2)	1.512 (8)
C(1)-C(2)	1.507 (9)	C(1)-P(1)	1.800 (8)
O(2)-C(3)	1.415 (11)		

Table 9.7 Bond angles (°)

Cl(1)-Hg(1)-Cl(2)	100.3(1)	Cl(1)-Hg(1)-C(1)	101.5(2)
Cl(2)-Hg(1)-C(1)	142.2(2)	Cl(1)-Hg(1)-Cl(1A)	88.8(1)
Cl(2)-Hg(1)-Cl(1A)	97.1(1)	C(1)-Hg(1)-Cl(1A)	113.7(2)
Hg(1)-Cl(1)-Hg(1A)	91.2(1)	C(11)-C(16)-P(1)	119.7(2)
C(15)-C(16)-P(1)	120.3(2)	C(21)-C(26)-P(1)	120.8(2)
C(25)-C(26)-P(1)	119.2(2)	C(31)-C(36)-P(1)	120.0(1)
C(35)-C(36)-P(1)	120.0(1)	C(41)-C(46)-C(2)	122.6(3)
C(45)-C(46)-C(2)	117.3(3)	Hg(1)-C(1)-C(2)	102.2(6)
Hg(1)-C(1)-P(1)	111.0(3)	C(2)-C(1)-P(1)	115.4(5)
O(1)-C(2)-C(46)	120.6(5)	O(1)-C(2)-C(1)	121.0(6)
C(46)-C(2)-C(1)	118.4(5)	C(16)-P(1)-C(26)	108.3(2)
C(16)-P(1)-C(36)	107.5(3)	C(26)-P(1)-C(36)	107.7(2)
C(16)-P(1)-C(1)	106.9(3)	C(26)-P(1)-C(1)	113.0(3)
C(36)-P(1)-C(1)	113.2(2)		

for [(Ph_3P)CHCOPh·HgI_2]

Table 9.8 Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2 x10^3$)

	x	y	z	U(eq)
Hg(1)	5530(1)	552(1)	5277(1)	26(1)
I(1)	4630(1)	161(1)	6144(1)	24(1)
I(2)	6097(1)	698(1)	7125(1)	45(1)
P(1)	5384(1)	4190(1)	2707(2)	20(1)
O(1)	6186(2)	1687(2)	5026(7)	29(4)
C(1)	5560(3)	1119(3)	4230(9)	19(2)
C(2)	5804(4)	1458(4)	5115(10)	24(3)
C(11)	5507(3)	4508(2)	294(6)	31(3)
C(12)	5561	4802	-629	36(3)
C(13)	5583	5179	-284	35(3)
C(14)	5551	5263	984	34(3)
C(15)	5497	4969	1908	27(3)
C(16)	5476	4591	1563	22(2)
C(21)	6477(2)	2006(2)	2238(6)	26(3)
C(22)	6650	2428	1902	37(3)
C(23)	6387	2585	1553	33(3)
C(24)	5951	2318	1539	35(3)
C(25)	5778	1896	1875	29(3)
C(26)	6041	1740	2224	22(2)
C(41)	5136(2)	1334(2)	6270(5)	28(3)
C(42)	4948	1410	7306	31(3)
C(43)	5198	1672	8282	32(3)
C(44)	5635	1857	8223	35(3)
C(45)	5823	1781	7187	33(3)
C(46)	5573	1520	6211	22(2)
C(31)	6212(2)	800(3)	1641(6)	37(3)
C(32)	6501	659	1610	45(3)
C(33)	6778	746	2616	50(4)
C(34)	6765	973	3655	44(3)
C(35)	6475	1114	3687	31(3)
C(36)	6198	1027	2680	29(3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 9.9 Bond lengths (Å)

Hg(1)-I(1)	3.010 (1)	Hg(1)-I(2)	2.705 (1)
Hg(1)-C(1)	2.311 (12)	Hg(1)-I(1A)	2.812 (1)
I(1)-Hg(1A)	2.812 (1)	P(1)-C(16)	1.803 (8)
P(1)-C(1A)	1.806 (10)	P(1)-C(26A)	1.812 (4)
P(1)-C(36A)	1.810 (9)	O(1)-C(2)	1.224 (13)
C(1)-C(2)	1.453 (14)	C(1)-P(1A)	1.806 (10)
C(2)-C(46)	1.518 (15)	C(26)-P(1A)	1.812 (8)
C(36)-P(1A)	1.810 (11)		

Table 9.10 Bond angles (°)

I(1)-Hg(1)-I(2)	115.1(1)	I(1)-Hg(1)-C(1)	97.0(3)
I(2)-Hg(1)-C(1)	118.8(2)	I(1)-Hg(1)-I(1A)	92.9(1)
I(2)-Hg(1)-I(1A)	110.8(1)	C(1)-Hg(1)-I(1A)	118.3(2)
Hg(1)-I(1)-Hg(1A)	87.1(1)	C(16)-P(1)-C(1A)	108.2(4)
C(16)-P(1)-C(26A)	106.8(4)	C(1A)-P(1)-C(26A)	109.9(3)
C(16)-P(1)-C(36A)	108.0(3)	C(1A)-P(1)-C(36A)	112.8(4)
C(26A)-P(1)-C(36A)	110.8(3)	Hg(1)-C(1)-C(2)	101.1(8)
Hg(1)-C(1)-P(1A)	110.9(7)	C(2)-C(1)-P(1A)	113.4(7)
O(1)-C(2)-C(1)	122.7(11)	O(1)-C(2)-C(46)	119.3(9)
C(1)-C(2)-C(46)	118.0(9)	P(1)-C(16)-C(11)	118.1(3)
P(1)-C(16)-C(15)	121.9(3)	C(21)-C(26)-P(1A)	120.6(3)
C(25)-C(26)-P(1A)	119.3(3)	C(2)-C(46)-C(41)	123.5(4)
C(2)-C(46)-C(45)	116.5(4)	C(31)-C(36)-P(1A)	118.8(2)
C(35)-C(36)-P(1A)	121.2(2)		

9.3 Results and Structure Descriptions

9.3.1 (Ph_3P)CHCOPh(1)

The crystal structure analysis confirmed that the phosphorane (**1b**), rather than phosphonium salt (**1a**), is the correct form in the crystal state, and it also revealed that there are two independent molecules in one cell (Figure 9.2).

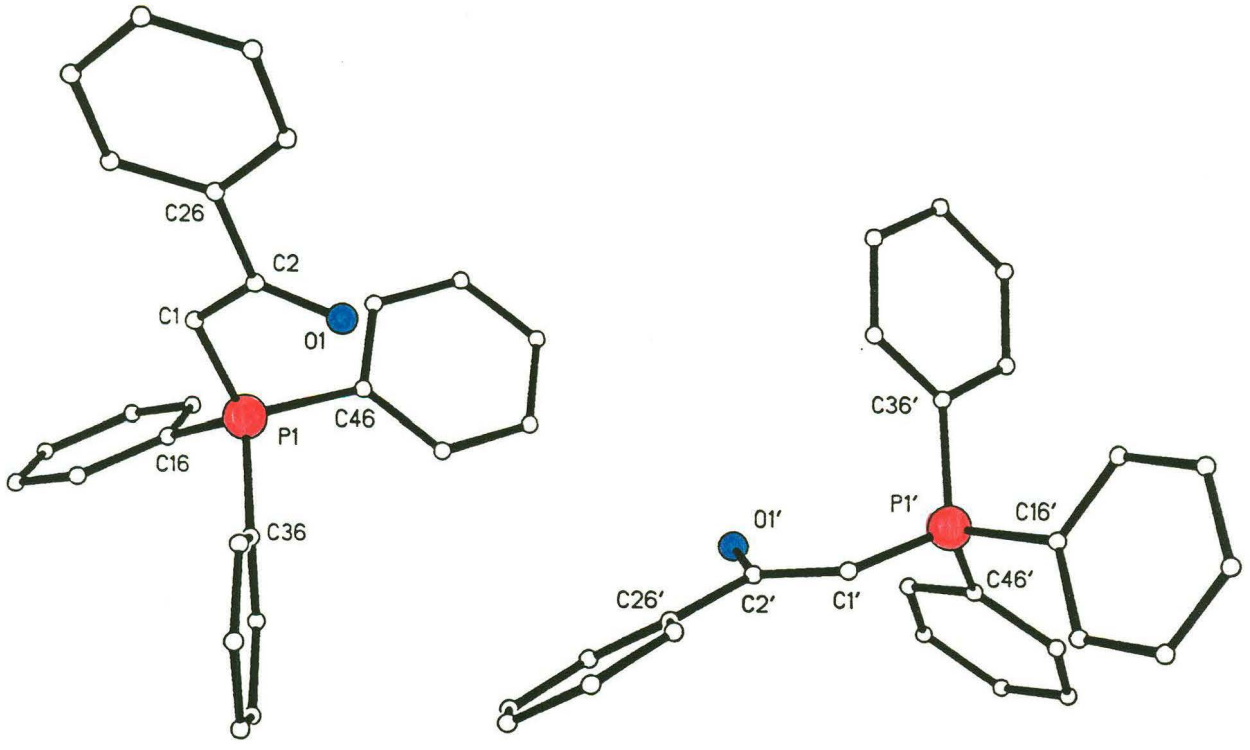


Figure 9.2 The perspective diagram of (Ph_3P)CHCOPh

Bond angles (Table 9.4) within the range of 105-116° for C-P-C fragments show that the phosphorus atoms P1 and P1' have approximately tetrahedral coordination stereochemistry which is consistent with the

phosphorane assignments. Bond angles of 115.4° and 123.1° for P(1)-C(1)-C(2) and P(1')-C(1')-C(2'), respectively, indicate a distorted trigonal arrangement about C1 and C1'.

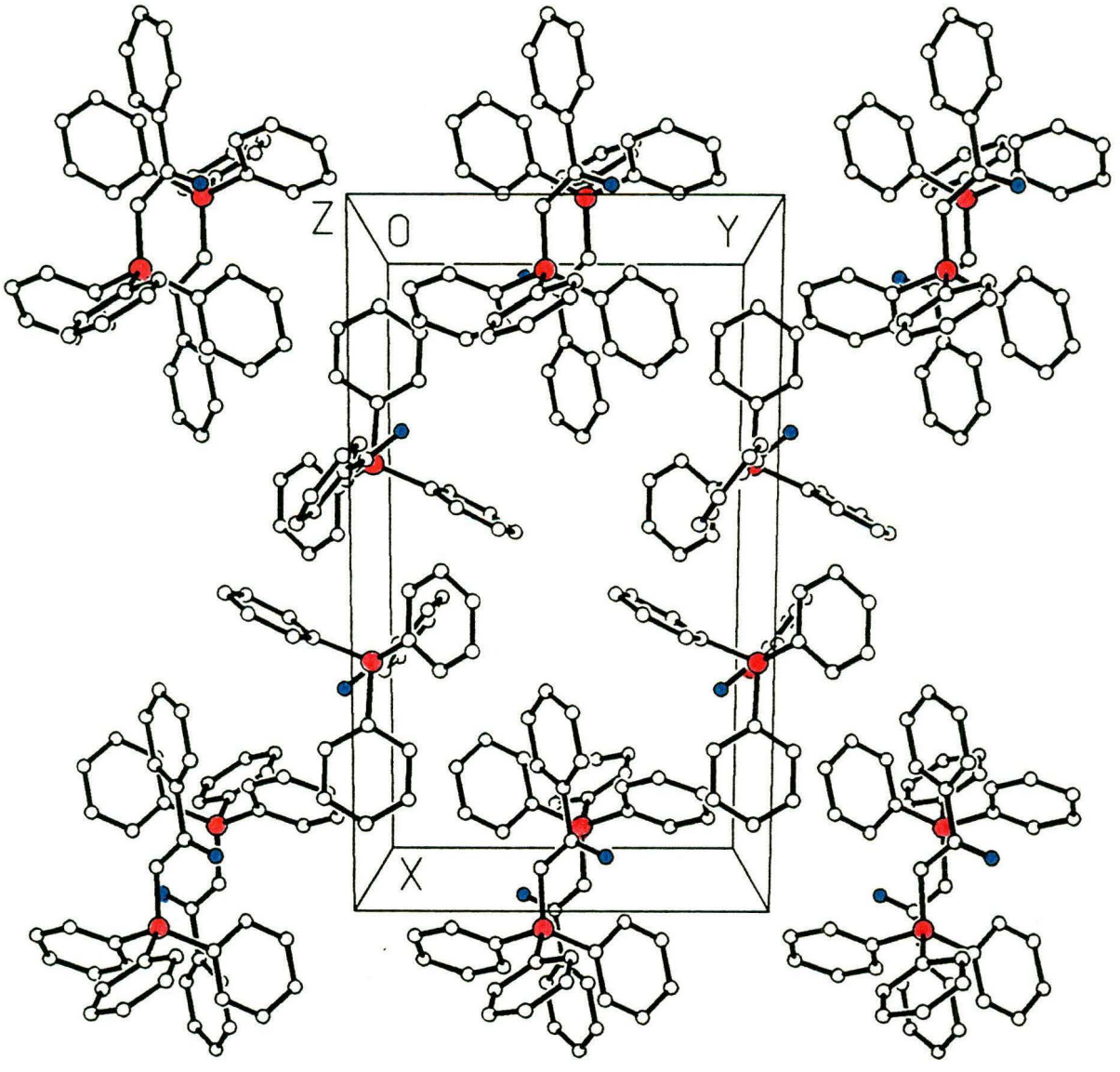


Figure 9.3 The packing diagram of $(Ph_3P)CHCOPh$

The P(1)-C(1) and P(1')-C(1') bond lengths of 1.716(5) and 1.723(5)Å (Table 9.3), respectively, are shorter than the other P-C bonds (1.800-1.815Å) showing partial double bond character. The P(1)-C(1) and P(1')-C(1') bond lengths are also shorter than the equivalent bond length of 1.753(4)Å reported for the phosphorane extensively stablized by two electron-withdrawing carbonyl groups [108] (Figure 9.1) and longer than the equivalent one of 1.66Å reported for the non-stablized methylide [107] (**1b**). There are delocalized systems at O(1)-C(2)-C(1)-P(1) and O(1')-C(2')-C(1')-P(1') (Figure 9.2). The comparatively short C(1)-C(2) [1.406(8)Å], C(1')-C(2') [1.398(8)Å] bonds and comparatively longer C(2)-O(1) [1.262(6)Å], C(2')-O(1') [1.245(6)Å] bonds are also consistent with extensive delocalization. The torsion angles of O(1)-C(1)-C(2)-P(1) and O(1')-C(1')-C(2')-P(1') are 0.8 and -2.2°, respectively. The deviations from planarity are very slight and show that the distortions of C(1) and C(1') atoms are minimal. The two parts P(1) C(1) C(2) O(1) C(26) and P(1') C(1') C(2') O(1') C(26') of the two independent molecules can be superimposed when the maximum distance between topologically equivalent atoms is 0.14Å. A packing diagram for this compound is shown in Figure 9.3.

9.3.2 $[(Ph_3P)CHCOPh{\cdot}HgCl_2]{\cdot}CH_3OH$ (2)

X-ray crystal structure analysis shows that the 1:1 complex adopts an centrosymmetrically dimeric arrangement in the solid state. Thus the best way to describe this complex is $[(Ph_3P)CHCOPh{\cdot}HgCl_2]_2{\cdot}2CH_3OH$ (Figure 9.4).

It is shown clearly in the diagram that two solvent methanol (CH_3OH) molecules exist symmetrically in the crystal accompanied by the crystallization of the dimer $[(Ph_3P)CHCOPh{\cdot}HgCl_2]_2$. In the solid state, the most electron density for the uncomplexed phosphorane is localized at C(1)

and C(1') and the σ bond to Hg(II) is localized at C(1) in this dimeric complex.

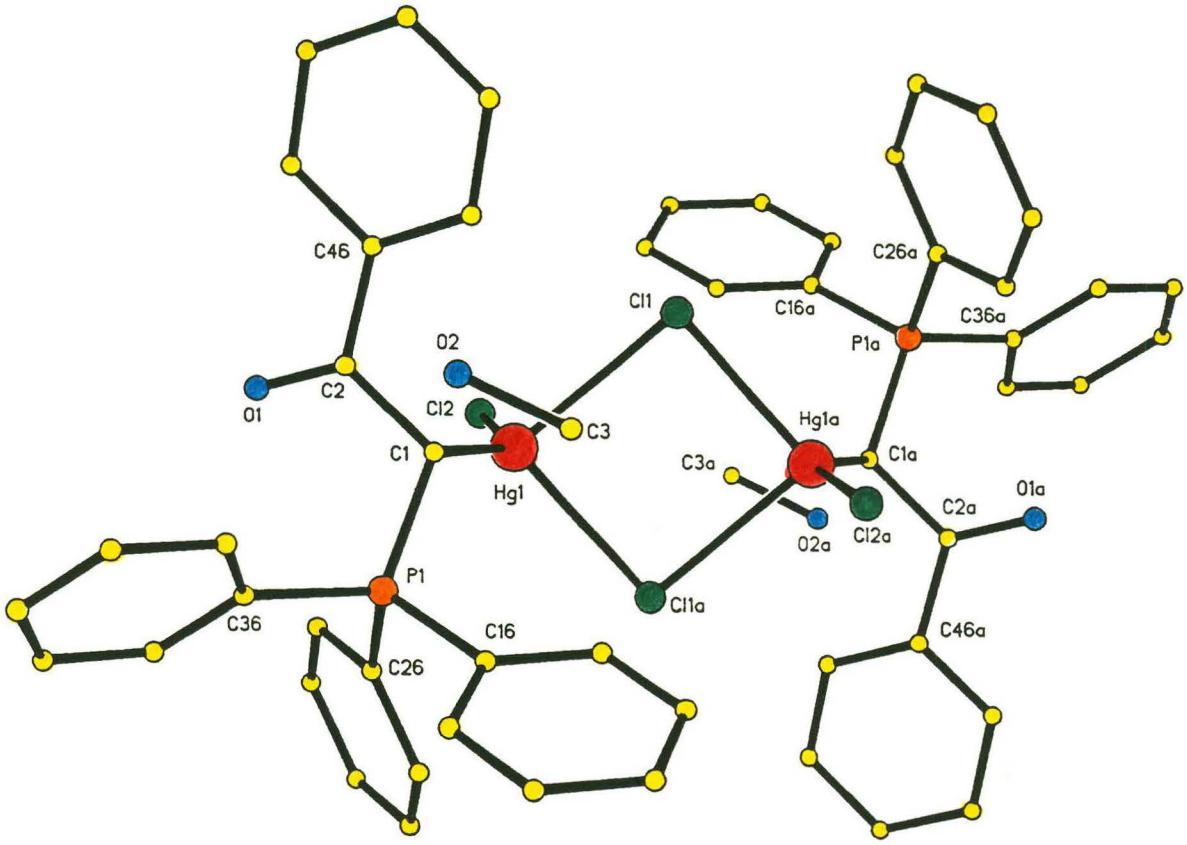


Figure 9.4 The perspective diagram for $[(Ph_3P)CHCOPh{\cdot}HgCl_2]_2{\cdot}2CH_3OH$

The C(1) atom in the complex has a distorted tetrahedral coordination environment with the Hg-C distance at 2.214(9)Å which is longer than the "standard" Hg-C bond length of 2.06-2.09Å [109-113]. Hence, the

electronegative substituent chlorine atoms in this compound have induced some elongation of the Hg-C bonds. This can result from both steric strains and the influence of the Hg atom coordination environment. However steric strains can only cause a small elongation of the Hg-C bond in the range of 2.06-2.15Å [114, 115]. We consider that the elongation of the Hg-C bonds must be largly due to the coordination environment of the Hg atoms and the participation of the secondary interactions. The Hg(II) in this complex also has a roughly tetrahedral coordination environment, with one short Hg-Cl bond [Hg(1)-Cl(2) 2.416(3)Å], one Hg-C bond [Hg(1)-C(1) 2.214(9)Å] and two asymmetric, intermediately strong bridging Hg-Cl bonds at the distances of 2.625(2)Å and 2.709(2)Å, respectively. The Hg(II) also shows the tendency to retain linearity as two short bonds Hg(1)-C(1) [2.214(9)Å] and Hg(1)-Cl(2) [2.416(3)Å] can be easily distinguished with the large angle in between [142.2(2)°]. The slightly asymmetric Hg-Cl bridging system in this complex is very similar to those found in isolated $Hg_2Cl_6^{2-}$ dimeric moiety (Chapters 4 and 5). It is also in agreement with the bridging system found in the complex of $[(S)_s(S)_c$–Me(EtCHPhCH$_2$)S·$HgCl_2]_2$ [116]. The two bridging Hg-Cl bonds [2.625(2)Å and 2.709(2)Å] in $[(Ph_3P)CHCOPh{\cdot}HgCl_2]_2{\cdot}2CH_3OH$ may be regarded as secondary bonds [3]. Under the influence of the secondary bonds a distortion of the C-Hg-Cl unit occurs accompanied by the elongation of the Hg-C bond. In the complex, C(1)-C(2) bond length is 1.507(9)Å and is significantly longer than the corresponding bond found in the uncomplexed phosphorane (~1.40Å). However the C(2)-O(1) distance of 1.229(8)Å is slightly shorter than those found in the isolated ligand (~1.25Å). These observations may be explained as due to the complexation of $HgCl_2$ with C(1); the delocalized system of O(1)-C(2)-C(1)-P(1) in the isolated phosphorane is destroyed so that the partial double bond character of C(1)-C(2) vanishes and the double bond character of C(2)-O(1) shows very strongly in the complex. Also, after being complexed with $HgCl_2$ at the C(1) position, the partial double bond

character showing in the isolated phosphorane disappears as well. Thus the P(1)-C(1) bond elongates from 1.72Å [1.716(5) and 1.723(5)Å] to 1.800(4)Å and the P(1) atom has a coordination environment much closer to tetrahedral in the complex than that in the uncomplexed phosphorane. Compared with the isolated ligand the remainder part of the molecule almost stays the same.

9.3.3 [$(Ph_3P)CHCOPh{\cdot}HgI_2$] (3)

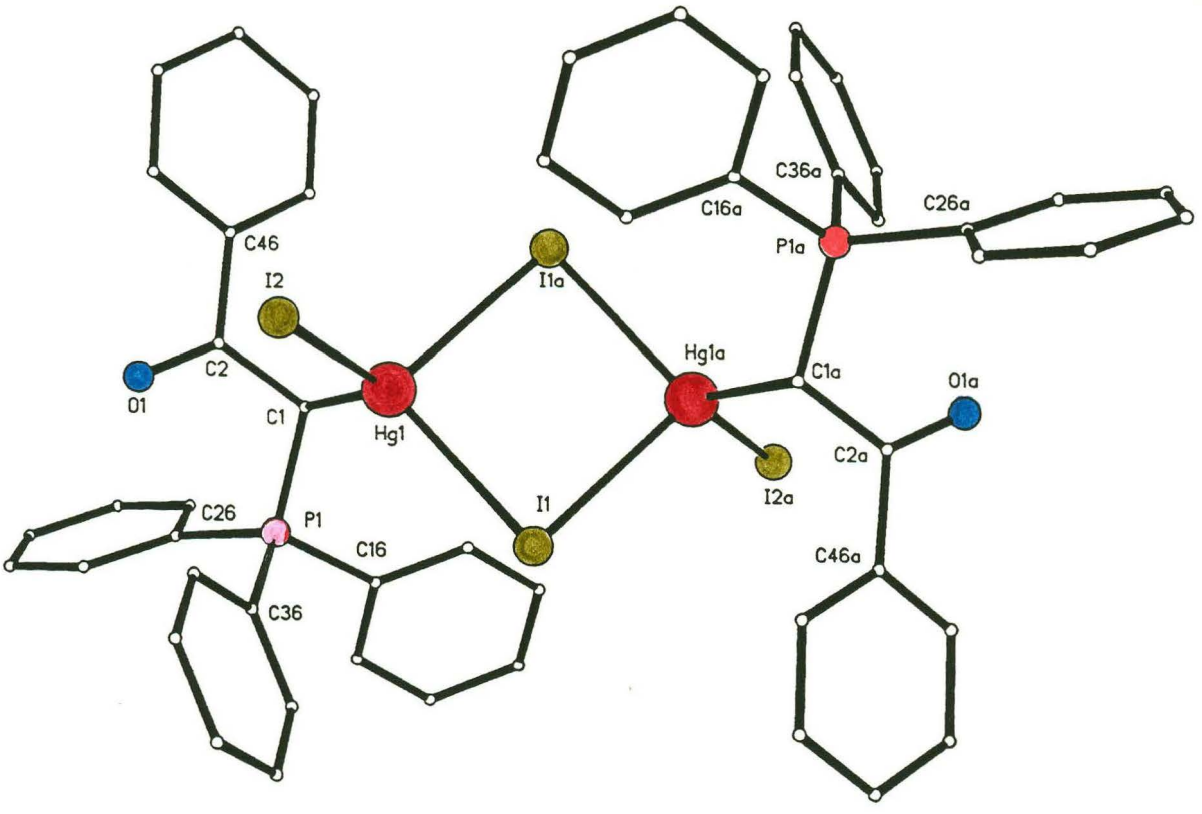


Figure 9.5 The perspective diagram for $[(Ph_3P)CHCOPh{\cdot}HgI_2]_2$

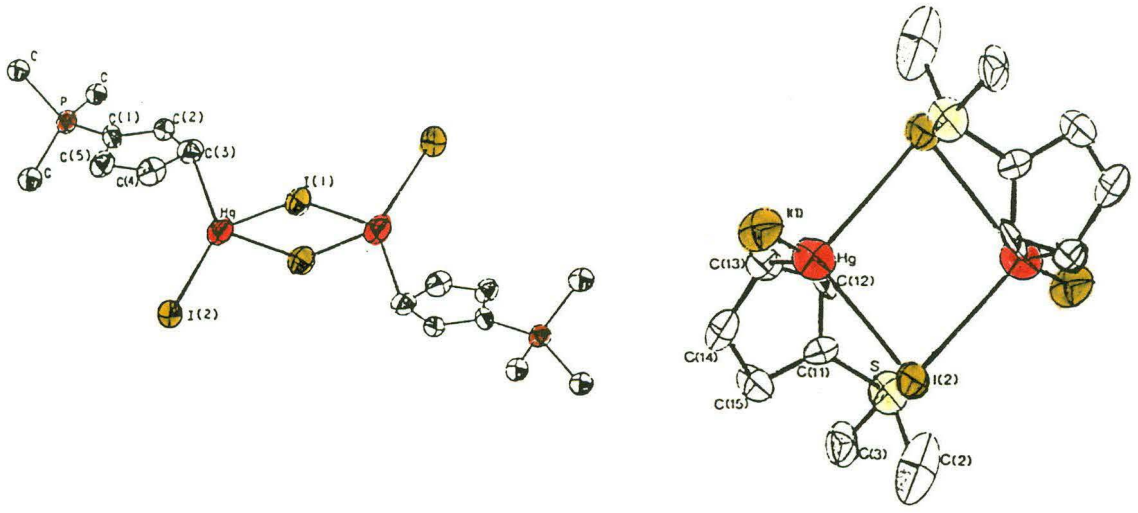
This molecule adopts a structure similar to that of the $HgCl_2$ adduct, but with HgI_2, the bridging Hg-I bonds [2.812(1)Å and 3.010(1)Å] are more asymmetrical that those in the $HgCl_2$ adduct (Figure 9.5).

The iodine-bridging system found in this complex is similar to those found in the crystal structures of $[(Ph_3P)C_5H_4HgI_2]$ [117] and $[(Me_2S)C_5H_4HgI_2]$ [118]. The Hg(II) ion also has a roughly tetrahedral coordination with the Hg-C distance at 2.311(12)Å and Hg-I distances at 3.010(1), 2.705(1) and 2.812(1)Å, respectively. However in this structure, the tendency of the Hg atom to retain the sp-hybridized state does not show as strongly as in the structure (**2**). The two shorter bonds Hg(1)-C(1) (2.311(12)Å) and Hg(1)-I(2) (2.705(1)Å) are distinguishable with the angle between them C(1)-Hg(1)-I(2) 118.8(2)° but the shortest Hg-I bond 2.705(1)Å is not very much shorter than the second shortest one (2.812(1)Å). We may consider, here, both of the Hg-I bonds as normal Hg-I bonds and the third one [3.010(1)Å] as a secondary Hg-I interaction. It is also shown that in the crystal structure of (**3**), the Hg atom coordination environment is much closer to tetrahedral than that in the topologically equivalent molecular structure of (**2**). The angles between the atoms coordinated to the Hg are 115.1(1), 118.8(2), 110.8(1), 97.0(3), 92.9(1) and 118.3(2)°, respectively.

This crystal structure is an exception from the tendency of the Hg(II) to retain the sp-hybridized state.

There are a few other examples of organomercury compounds with a distorted tetrahedral coordination of the Hg atom other than linear. Crystal structures (**4**) [117] and (**5**) [118] are two of the examples (Figure 9.6).

In these two compounds Hg(II) shows a strong tendency to retain the sp-hybridized state, as we found in the structure (**2**). In both examples, two shortest bonds Hg-C (2.29(1) and 2.20(1)Å) and Hg-I (2.681(1) and 2.706(1)Å) are distinguishable with the largest angle between them (131.5(2) and 133.6(4)°, respectively). The other Hg-I bonds (2.937(1), 2.982(1) and 2.896(1), 3.031(1)Å) can be considered as secondary bonds [3].



(4) (5)

Figure 9.6 The structures of compounds $[(Ph_3P)C_5H_4{\cdot}HgI_2]_2$ (**4**) and $[(CH_3)_2SC_5H_4{\cdot}HgI_2]_2$ (**5**)

9.4 Conclusion

As we have mentioned many times before, one of the characteristic features of the mercury(II) ion is to form two strong and dominant bonds; even if some further ligands are added it shows the tendency to retain the linear coordination. However as we have found in both inorganic and organic mercury(II) compounds that the Hg(II) atom also can take a very wide range of coordination environments. This has led the stereochemistry of mercury(II) being interesting and contentious.

Abbreviations

$$R = \frac{\Sigma \left(\left| |F_o| - |F_c| \right| \right)}{\Sigma |F_o|}$$

$$R_w = \frac{\Sigma \sqrt{w} \left(\left| |F_o| - |F_c| \right| \right)}{\Sigma \sqrt{w} |F_o|}$$

EDTA: ethylenediaminetetraacetic acid $(HOOCH_2C)_2N(CH_2)_2N(CCH_2OOH)_2$

Me: methyl group $-CH_3$

Et: ethyl group $-CH_2CH_3$

en: ethylenediamine $NH_2(CH_2)_2NH_2$

trien: triethylenetetramine $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$

Ph: phenyl group $-C_6H_5$

DABCO: 1,4-diazabicyclo [2, 2, 2]-octan $[(CH_2)_6N_2H_2]^{2+}$

Appendix A

ATOMIC COORDINATES AND LABELLING SCHEMES

Table 1 Atomic coordinates ($x10^4$) for $[Et_4N]Hg_6Cl_{13}$

	x	y	z
Hg(1)	1692(1)	4790(1)	2285(1)
Cl(3)	3333	6667	1667
Cl(1)	3120(8)	4870(8)	2758(3)
Cl(2)	167(9)	4519(9)	1831(4)
Hg(2)	1142(2)	9064(1)	615(1)
Cl(6)	0	0	0
Cl(4)	1898(14)	10659(11)	1071(4)
Cl(5)	545(8)	7432(8)	193(3)
N	6667	3333	383(45)

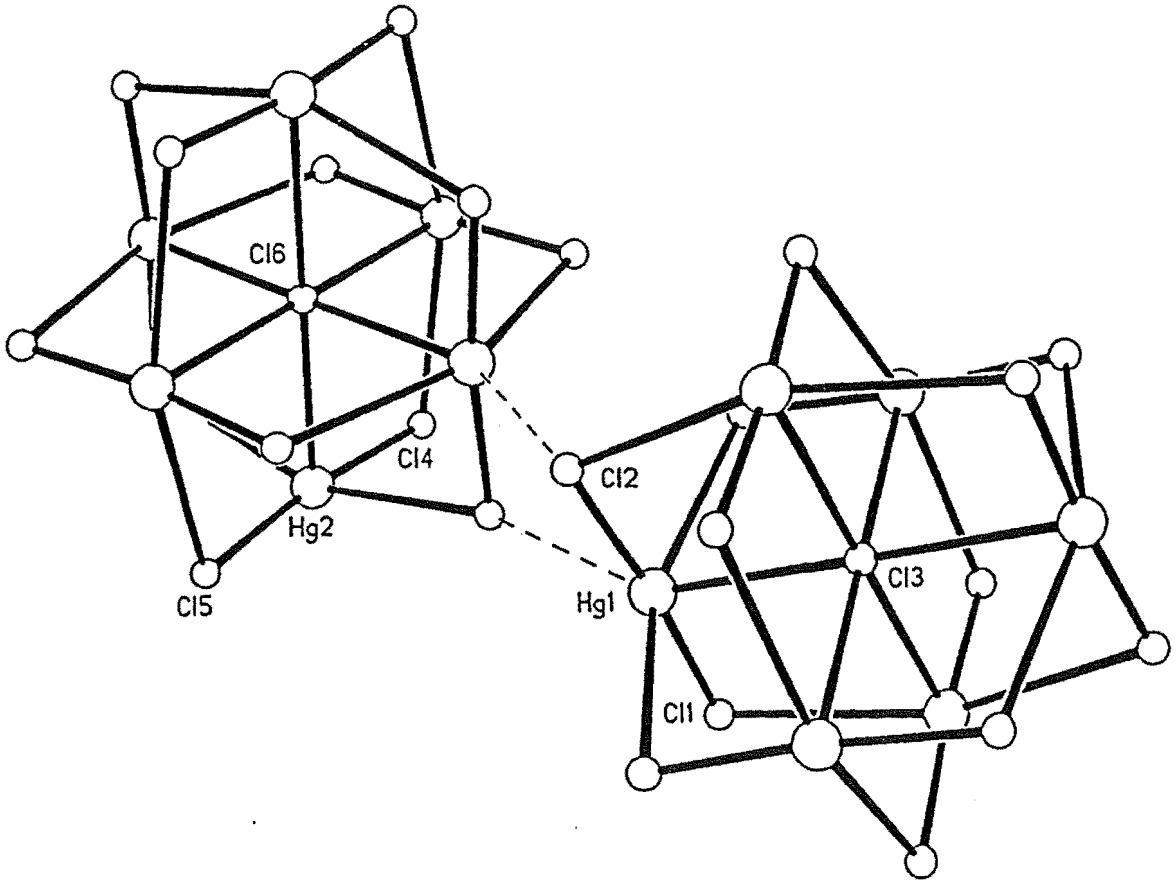
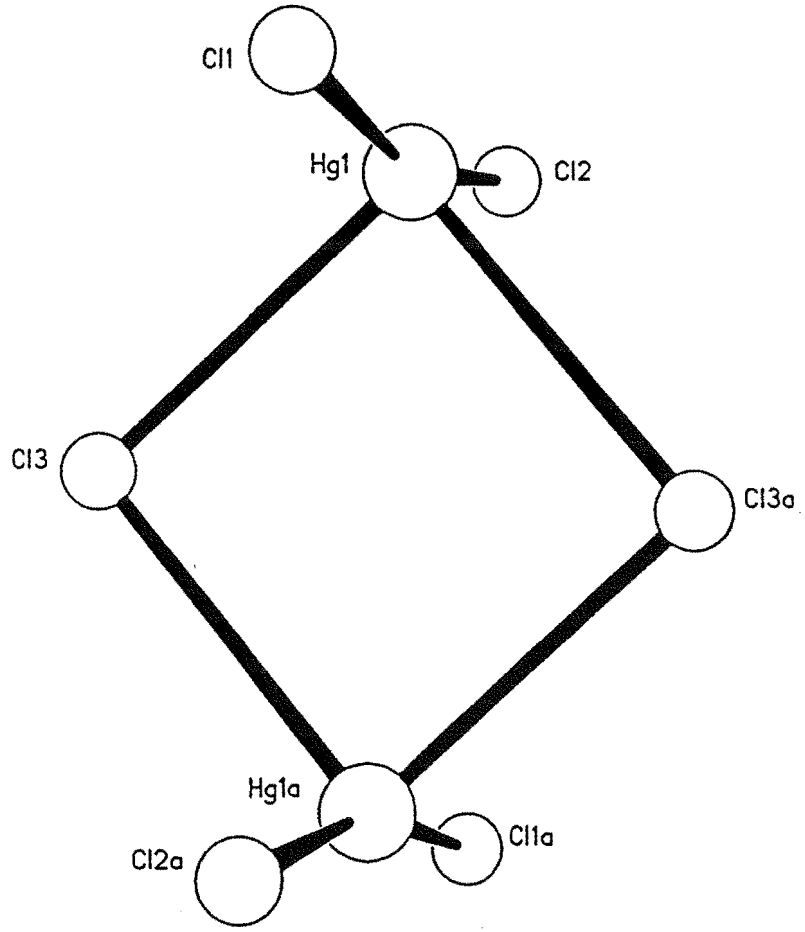


Table 2 Atomic coordinates ($x10^4$) for $[H_2en][Hg_2Cl_6]$

	x	y	z
Hg(1)	1723(1)	2048(1)	4343(1)
Cl(1)	597(7)	2925(6)	7025(5)
Cl(2)	1815(6)	1767(6)	1469(4)
Cl(3)	3821(7)	-2287(6)	5531(5)
N(1)	4762(20)	6642(19)	1649(15)
C(1)	4028(24)	6028(22)	168(19)



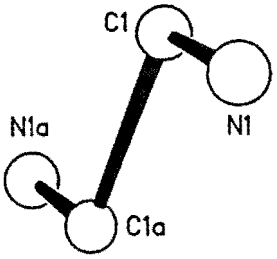


Table 3 Atomic coordinates (x10^4) for $[H_2en]_2[HgCl_4][Cl]_2$

	x	y	z
Hg(1)	1945(1)	1748(1)	2500
Cl(1)	3964(3)	1874(8)	2500
Cl(2)	1748(3)	-2871(6)	2500
Cl(3)	1495(2)	2097(4)	3668(1)
Cl(4)	4030(2)	2149(4)	4906(1)
N(1)	5008(8)	1363(16)	6392(5)
N(2)	6598(7)	2881(14)	5286(4)
C(1)	5735(9)	3229(20)	6422(5)
C(2)	6748(8)	2906(18)	6035(5)

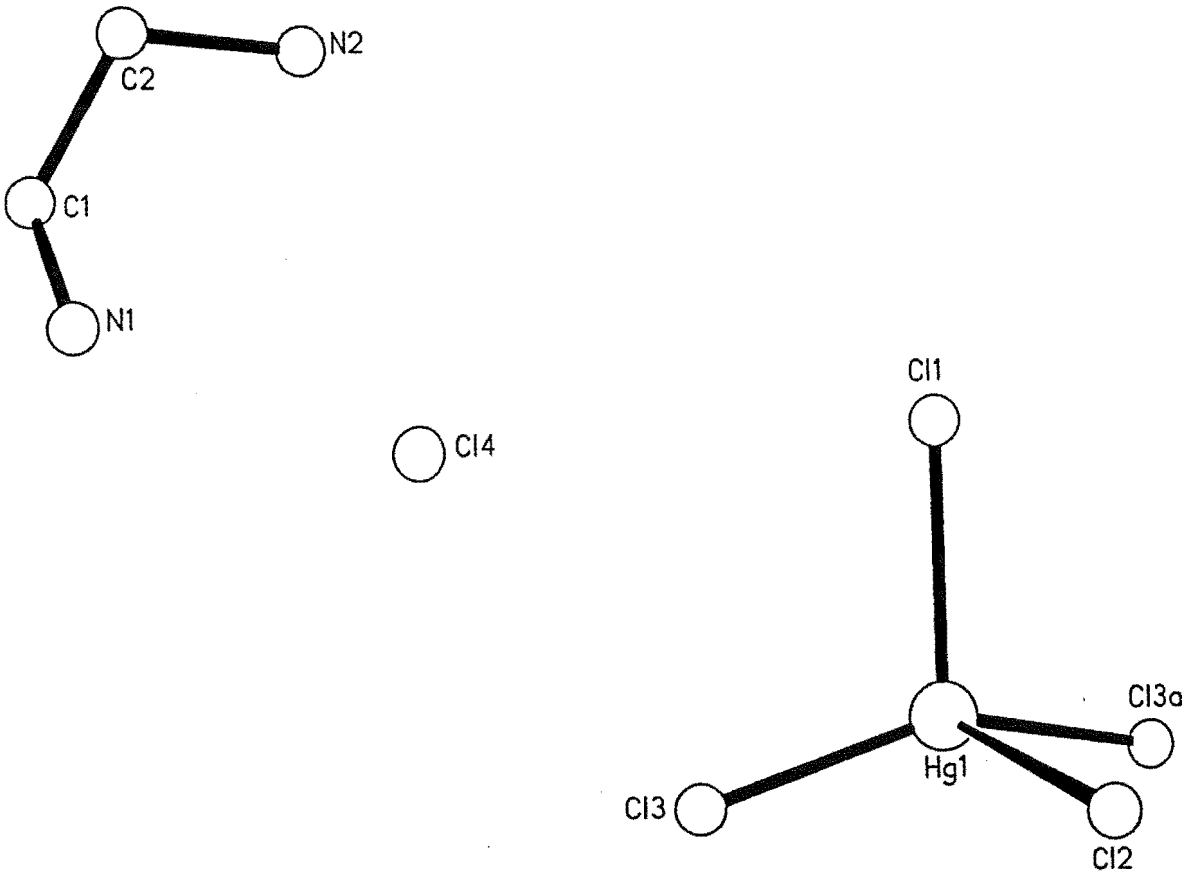


Table 4 Atomic coordinates (x10^4) for *trans*-$[CoCl_2(en)_2]_2[Hg_2Cl_6]$

	x	y	z
Hg(1)	3127(1)	811(1)	339(1)
Co(1)	5044(1)	-2821(1)	2631(1)
Cl(1)	5743(2)	680(3)	913(1)
Cl(2)	7435(2)	-2724(3)	2348(1)
Cl(3)	2627(2)	-2914(2)	2893(1)
Cl(4)	1477(2)	-1128(2)	772(1)
Cl(5)	2667(3)	3288(3)	-138(1)
N(1)	4548(8)	-2604(8)	1532(4)
N(2)	5060(8)	-5014(9)	2439(5)
C(1)	5094(11)	-5291(11)	1595(6)
C(2)	4097(10)	-4101(10)	1218(5)
N(3)	5023(8)	-642(8)	2817(4)
N(4)	5589(9)	-3035(8)	3723(4)
C(3)	4988(10)	-343(10)	3677(5)
C(4)	5950(10)	-1498(12)	4038(6)

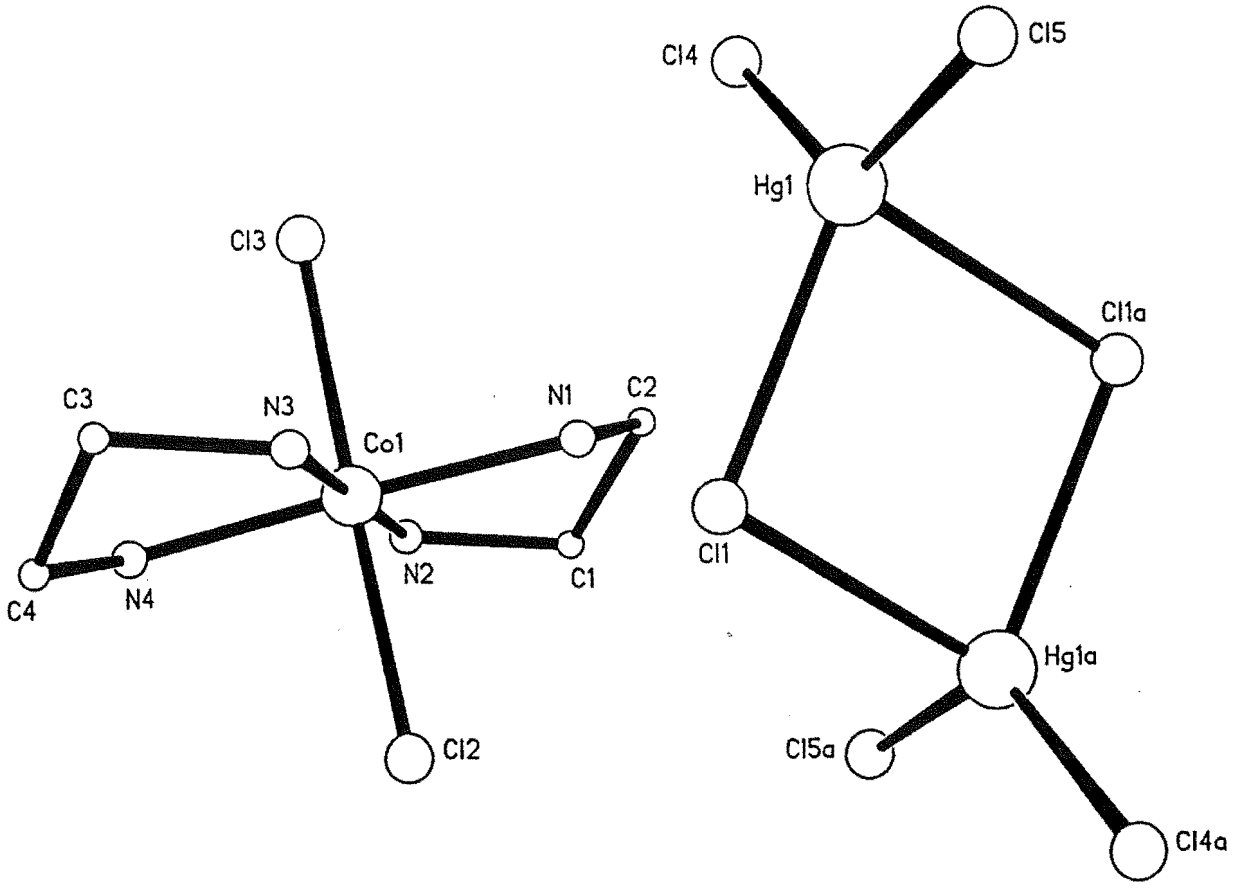


Table 5 Atomic coordinates (x10⁴) for $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$

	x	y	z
Hg(1)	1219(1)	1969(1)	4785(1)
Hg(2)	967(1)	1187(1)	1306(1)
Hg(3)	1381(1)	9771(1)	6285(1)
Co(1)	-3825(3)	1281(1)	-1988(2)
Cl(1)	865(7)	1657(2)	-630(3)
Cl(2)	-1305(7)	422(2)	1249(4)
Cl(3)	-1687(7)	1850(2)	4724(4)
Cl(4)	3901(6)	740(2)	1112(4)
Cl(5)	4110(6)	2069(2)	4966(4)
Cl(6)	1176(7)	2151(2)	2348(4)
Cl(7)	4223(6)	9516(2)	6177(4)
Cl(8)	1280(7)	11010(2)	6646(4)
Cl(9)	-1525(6)	9570(2)	6157(4)
O(1)	6060(21)	1856(5)	2343(12)
N(1)	-1995(20)	655(7)	-1705(12)
N(2)	-5620(19)	1911(6)	-2222(12)
N(3)	-4081(21)	963(7)	-3463(13)
N(4)	6423(21)	3411(7)	4507(13)
N(5)	4440(20)	4326(6)	3469(12)
N(6)	-2131(20)	1890(6)	-2483(12)

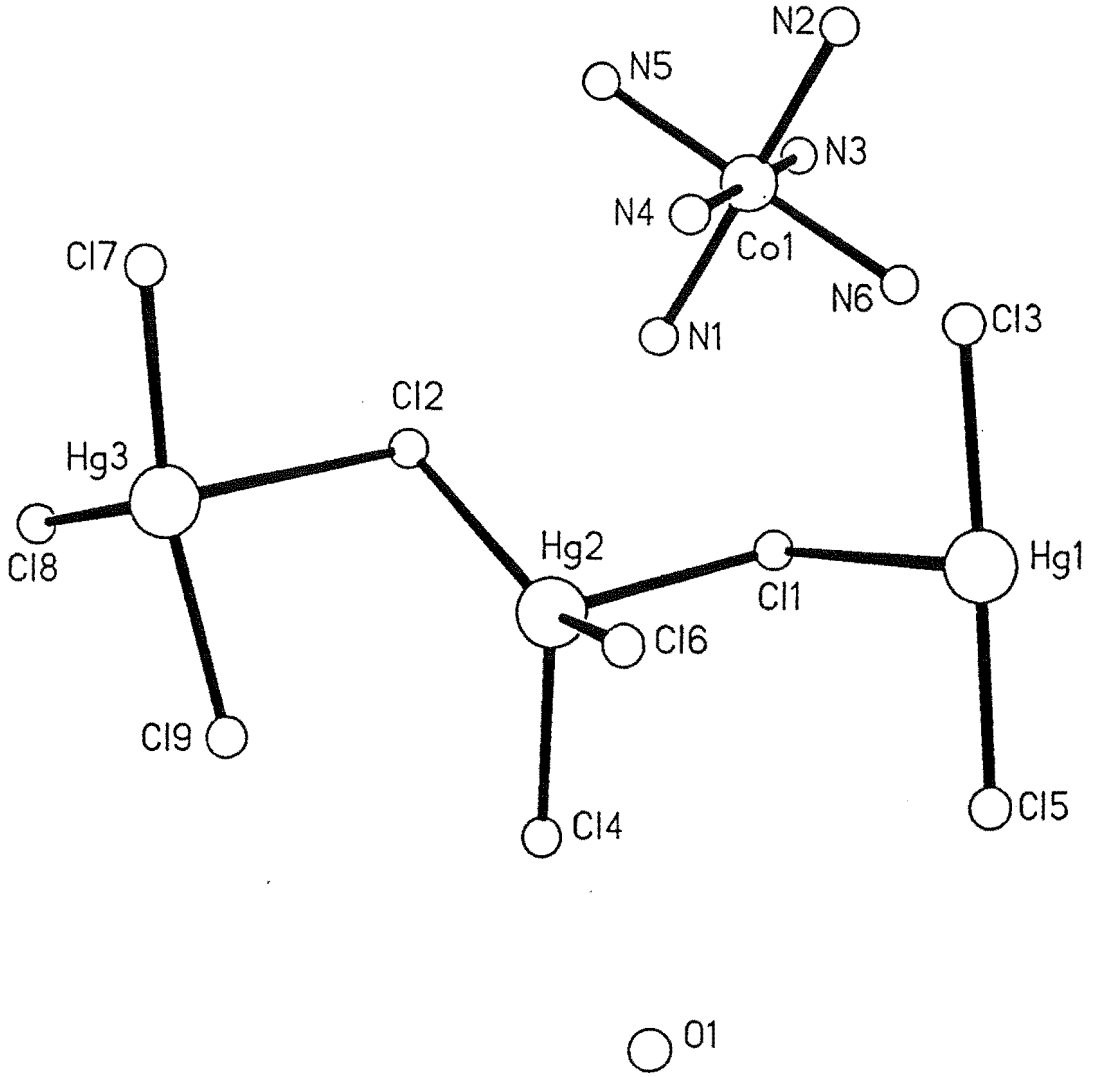


Table 6 Atomic coordinates (x10^4) for [H_4trien][Hg_2Cl_8]

	x	y	z
Hg(1)	2669(1)	1971(1)	1079(1)
Hg(2)	7596(1)	1760(1)	1327(1)
Cl(1)	5222(3)	1676(4)	1102(3)
Cl(2)	8117(4)	2007(4)	2995(3)
Cl(3)	7639(4)	3638(4)	527(3)
Cl(4)	2869(4)	464(4)	2194(3)
Cl(5)	2907(4)	3912(4)	1998(3)
Cl(6)	2623(4)	2821(4)	-457(3)
Cl(7)	7641(4)	211(4)	256(3)
Cl(8)	253(3)	1887(4)	855(3)
N(2)	282(14)	4520(12)	1272(9)
C(4)	4976(17)	4803(15)	9455(11)
C(1)	289(14)	4021(15)	2926(11)
C(3)	-89(14)	5301(14)	475(10)
N(4)	4742(13)	1074(12)	8832(10)
N(1)	-356(12)	4239(14)	3745(9)
C(2)	-157(14)	4802(14)	2132(11)
N(3)	5182(12)	3575(12)	9480(9)
C(5)	5226(14)	3111(16)	8519(10)
C(6)	5582(15)	1872(16)	8523(12)

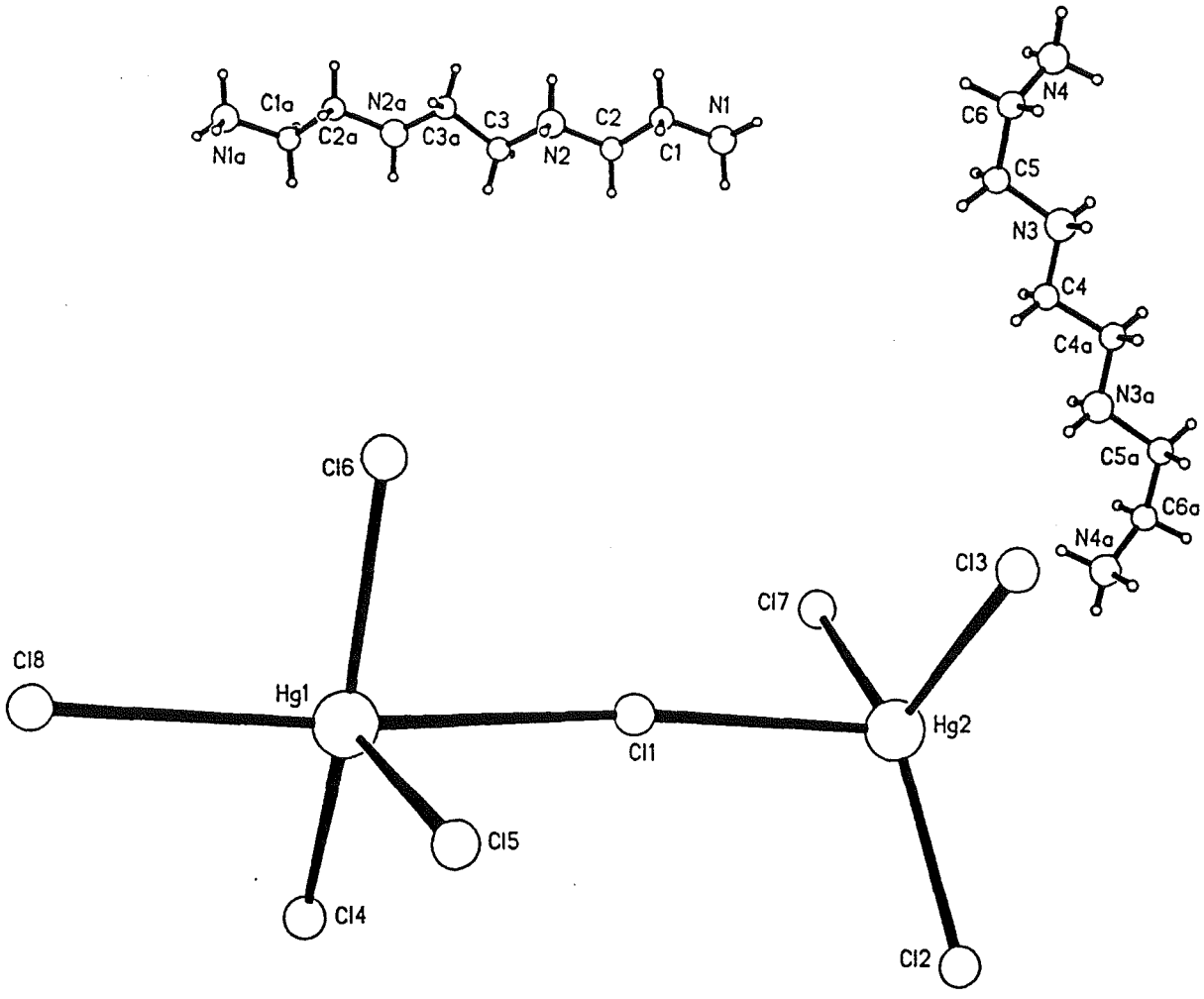


Table 7 Atomic coordinates (x10^4) for *cis*-$[PtCl_2(NH_3)_2][HgCl_2]_3$

	x	y	z
Hg(1)	0	0	0
Pt(1)	0	2399(1)	2500
Hg(2)	1996(1)	148(1)	-792(1)
Cl(1)	-637(2)	-2911(7)	342(3)
Cl(2)	1504(2)	-2669(7)	-60(4)
Cl(3)	2550(2)	2841(8)	-1540(4)
N(1)	788(9)	4608(25)	2312(13)
Cl(4)	853(2)	-83(7)	2250(3)

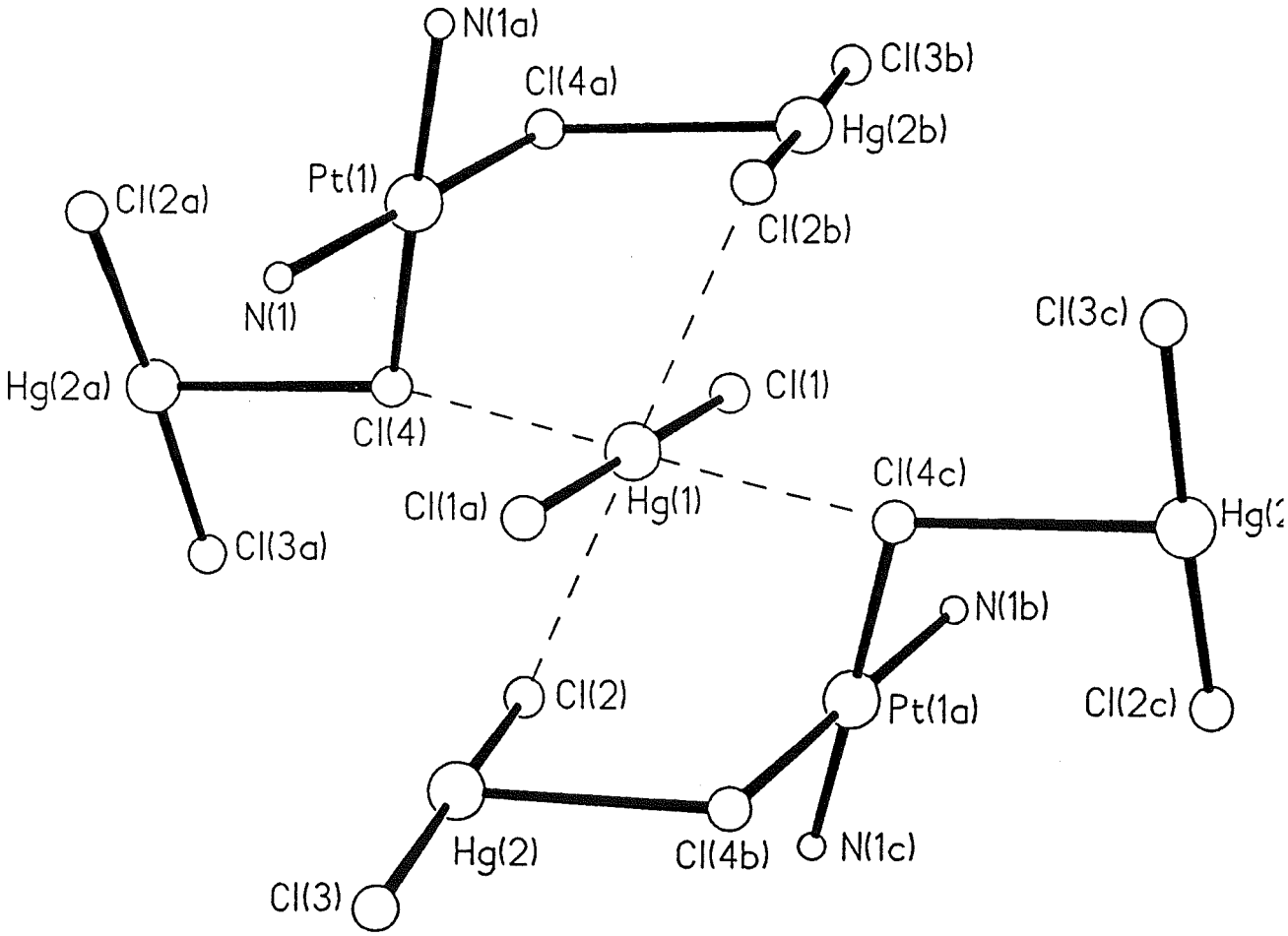


Table 8 Atomic coordinates (x10^4) for [(Ph_3P)CHCOPh]

	x	y	z
P(1)	1535(1)	-31(2)	775(1)
P(1')	5679(1)	5513(2)	1474(1)
O(1)	2005(2)	819(4)	-419(2)
O(1')	4509(2)	3904(4)	1875(2)
C(1)	1273(3)	-643(5)	-58(3)
C(2)	1569(3)	-74(6)	-564(3)
C(1')	4740(3)	5579(5)	1215(3)
C(2')	4292(3)	4771(5)	1463(3)
C(11)	435(2)	-1047(3)	1269(2)
C(12)	130	-1877	1652
C(13)	577	-2695	2115
C(14)	1330	-2683	2196
C(15)	1634	-1852	1813
C(16)	1187	-1034	1350
C(21)	765(2)	-1302(3)	-1570(2)
C(22)	566	-1647	-2279
C(23)	964	-1221	-2737
C(24)	1561	-449	-2486
C(25)	1759	-104	-1778
C(26)	1362	-530	-1320
C(21')	3172(2)	5698(3)	608(2)
C(22')	2424	5937	420
C(23')	1984	5480	831
C(24')	2292	4785	1431
C(25')	3040	4546	1619
C(26')	3479	5003	1208
C(45')	6492(2)	6723(3)	2686(2)
C(44')	6772	6845	3413
C(43')	6646	5933	3866
C(42')	6239	4899	3590
C(41')	5959	4777	2862
C(46')	6085	5689	2410
C(11')	5710(2)	7937(4)	1101(2)
C(12')	5886	8920	722
C(13')	6322	8733	258
C(14')	6582	7563	173
C(15')	6406	6580	552
C(16')	5970	6767	1016
C(35')	5654(1)	3357(3)	715(2)
C(34')	5973	2334	490
C(33')	6711	2084	779
C(32')	7130	2857	1293
C(31')	6812	3880	1517
C(36')	6073	4130	1228
C(31)	1127(2)	1892(3)	1537(2)
C(32)	783	3002	1594
C(33)	477	3689	991
C(34)	515	3267	330
C(35)	858	2156	273
C(36)	1164	1469	876
C(41)	2911(2)	-1000(3)	1047(2)
C(42)	3671	-986	1279
C(43)	4033	84	1561
C(44)	3635	1140	1611
C(45)	2875	1125	1378
C(46)	2513	55	1096

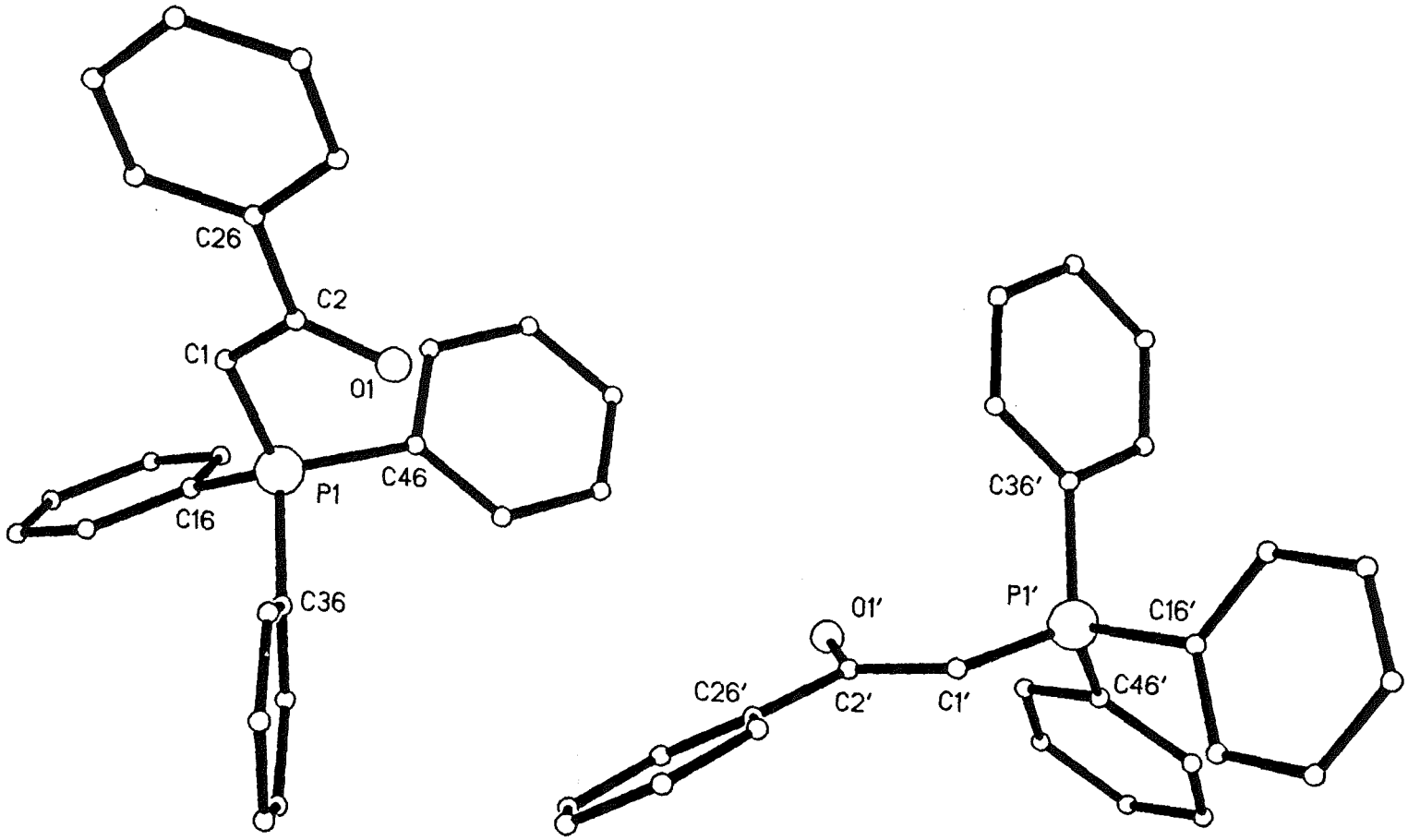

C26
C2
C1
O1
P1
C46
C16
C36
C36′
P1′
O1′
C16′
C26′
C2′
C1′
C46′

Table 9 Atomic coordinates (x10^4) for $[(Ph_3P)CHCOPh \cdot HgCl_2] \cdot CH_3OH$

	x	y	z
Hg(1)	-1743(1)	250(1)	1273(1)
Cl(1)	-957(2)	1584(2)	-699(1)
Cl(2)	-2962(2)	-1237(3)	1104(2)
O(1)	-4653(5)	2218(5)	3378(4)
C(11)	1425(4)	956(5)	1851(3)
C(12)	2839	1084	1521
C(13)	3191	1564	2199
C(14)	2128	1915	3206
C(15)	714	1787	3536
C(16)	362	1307	2858
C(21)	33(4)	-1764(4)	3650(4)
C(22)	149	-3207	3890
C(23)	-1049	-3657	4071
C(24)	-2364	-2663	4013
C(25)	-2480	-1220	3773
C(26)	-1282	-770	3592
C(31)	-3272(5)	1186(3)	5426(3)
C(32)	-4125	1839	6372
C(33)	-4353	3281	6388
C(34)	-3728	4070	5458
C(35)	-2875	3417	4512
C(36)	-2647	1975	4496
C(41)	-3318(3)	4569(4)	1043(3)
C(42)	-3883	5808	484
C(43)	-5420	6416	772
C(44)	-6392	5785	1618
C(45)	-5827	4545	2177
C(46)	-4290	3937	1889
C(1)	-2108(7)	1893(7)	2233(5)
C(2)	-3757(7)	2649(7)	2571(5)
P(1)	-1463(2)	1109(2)	3288(1)
O(2)	-1598(7)	5352(8)	2145(5)
C(3)	-65(11)	5026(10)	1532(8)

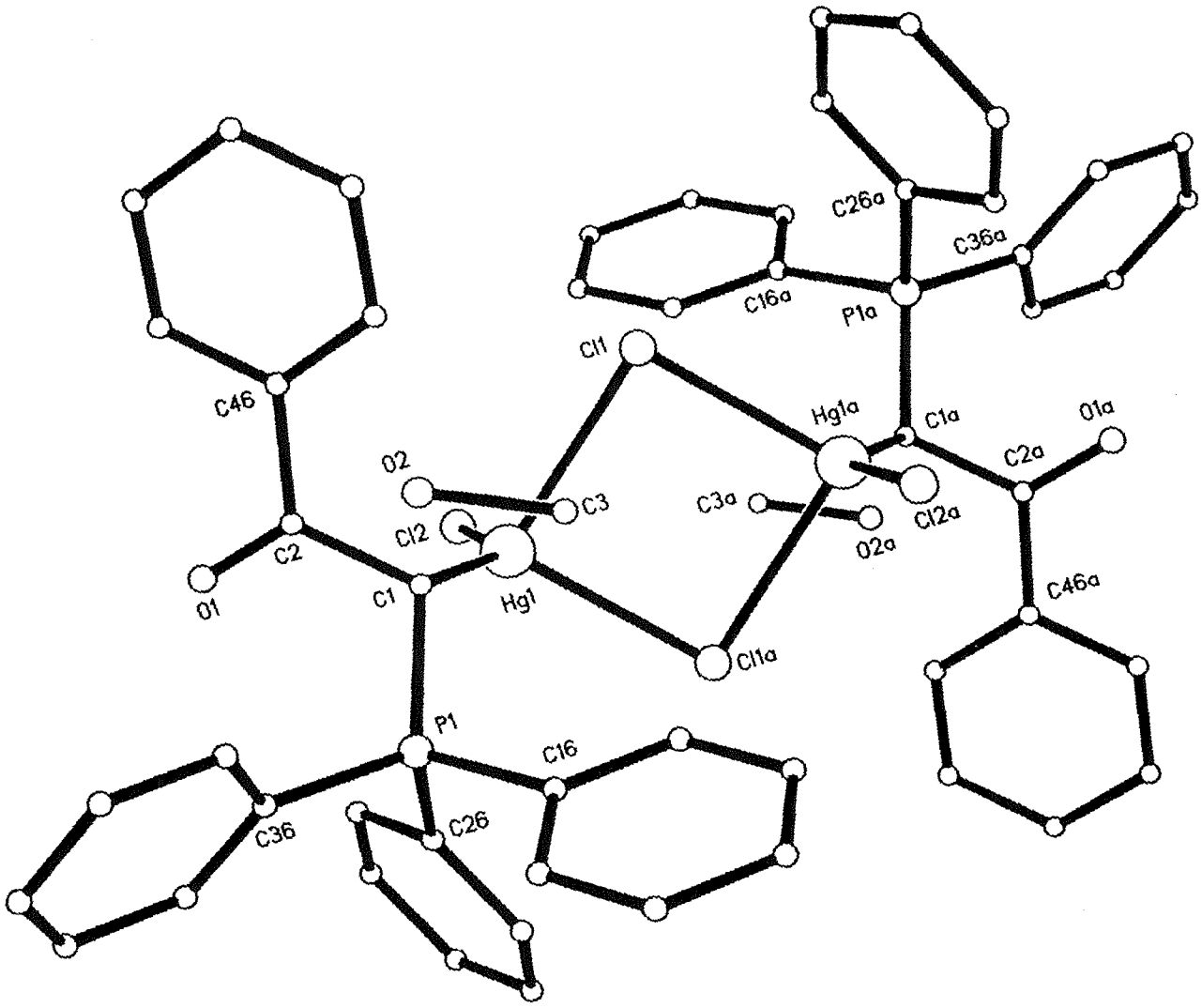
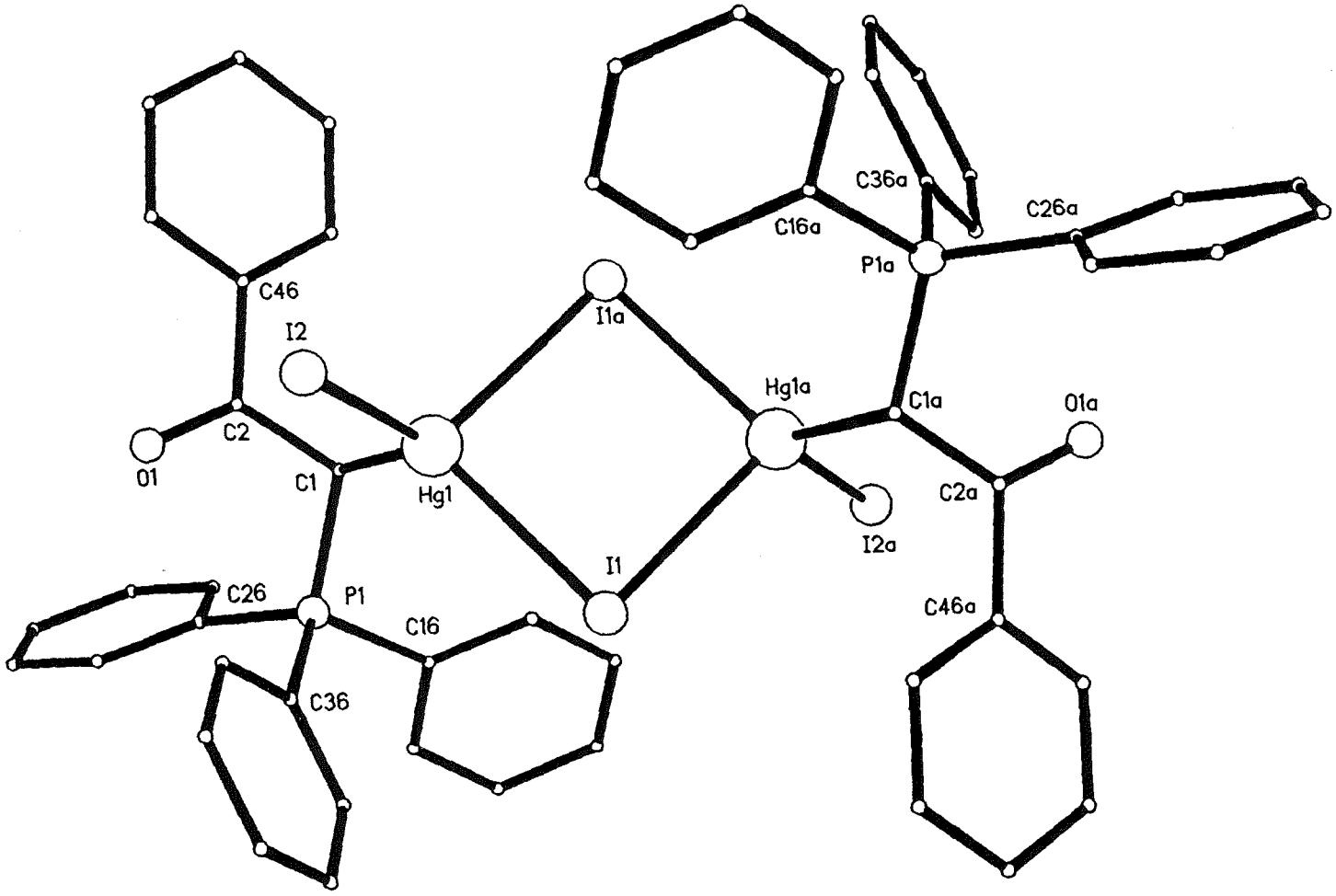

C26a
C36a
C16a
P1a
Cl1
C46
Hg1a
C1a
O1a
O2
C2a
C3a
C3
Cl2a
Cl2
O2a
C2
O1
C1
Hg1
C46a
Cl1a
P1
C16
C36
C26

Table 10 Atomic coordinates (x10^4) for [$(Ph_3P)CHCOPh \cdot HgI_2$]

	x	y	z
Hg(1)	5530(1)	552(1)	5277(1)
I(1)	4630(1)	161(1)	6144(1)
I(2)	6097(1)	698(1)	7125(1)
P(1)	5384(1)	4190(1)	2707(2)
O(1)	6186(2)	1687(2)	5026(7)
C(1)	5560(3)	1119(3)	4230(9)
C(2)	5804(4)	1458(4)	5115(10)
C(11)	5507(3)	4508(2)	294(6)
C(12)	5561	4802	-629
C(13)	5583	5179	-284
C(14)	5551	5263	984
C(15)	5497	4969	1908
C(16)	5476	4591	1563
C(21)	6477(2)	2006(2)	2238(6)
C(22)	6650	2428	1902
C(23)	6387	2585	1553
C(24)	5951	2318	1539
C(25)	5778	1896	1875
C(26)	6041	1740	2224
C(41)	5136(2)	1334(2)	6270(5)
C(42)	4948	1410	7306
C(43)	5198	1672	8282
C(44)	5635	1857	8223
C(45)	5823	1781	7187
C(46)	5573	1520	6211
C(31)	6212(2)	800(3)	1641(6)
C(32)	6501	659	1610
C(33)	6778	746	2616
C(34)	6765	973	3655
C(35)	6475	1114	3687
C(36)	6198	1027	2680


C36a
C16a
C26a
P1a
C46
I1a
I2
Hg1a
C1a
O1a
C2
O1
C1
Hg1
C2a
I2a
I1
C26
P1
C16
C46a
C36

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